Pyrolysis of coconut shell

M.Tech Thesis

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CERTIFICATE

This is to certify that the project report entitled **"Pyrolysis of Coconut shell"** is submitted by Tanmaya Kumar Rout (211CH1036) for the award of Master of Technology in Chemical Engineering at National Institute of Technology, Rourkela is prepared by him under my supervision and guidance.

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ABSTRACT

In the present scenario energy sectors and individual entrepreneurs can opt a new way of power generation using the most abundantly available renewable source of energy in the form of biomass wastes. Among the biomass resources coconuts are the abundant renewable resource of energy available all around the world. Literature review showed that limited research studies had been carried out on yielding the product from coconut shell pyrolysis. The objective of present work is to envisage the methodology of generating power by pyrolysis to obtain a high-grade of pyrolytic liquid that potentially could be used as a fuel or as feedstock to valuable chemicals. Pyrolysis is a thermal decomposition technique which decomposes carbonaceous bio wastes into liquids, gases, and char (solid residue) in the absence of oxygen.

The thermal degradation temperature range of the raw material was studied using thermo gravimetric analysis (TGA). In the initial phase of the study, experiments on pyrolysis of coconut shell were done for a temperature range of 450°C to 600°C to study the effect of temperature on various product yields. The liquid yield was highest for temperature of 575°C.

The oil samples obtained at optimum condition is analysed according to their fuel properties, elemental analysis, functional group presents, and compounds presents.

The solid residue was analysed. The char showed presence pores via SEM analysis. The char was used to prepare activated carbon.

The work also includes kinetic study of the degradation of the coconut shell.

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Chapter 1
Introduction

1. Introduction

Petroleum products such as fuel oil, gasoline or valuable chemicals are used in every aspect of life today. With rapid increase in world population, the demand for petroleum products is increasing day by day. But the world's oil supply is fixed since petroleum is naturally formed far too slowly in millions of years to be replaced at the rate at which it is being extracted [1]. Oil price also has increased over the years and it reached a record high of $145/barrel in 2008. As countries develop, industry and higher living standards drive up energy use, most often of oil. Thriving economies, such as India, is quickly becoming large oil consumers [2]. India's oil imports are expected to more than triple from 2005 levels by 2020, rising to 5 million barrels per day (790×10^3 m^3/d) [3].

With the concern of depletion rate and price increase, there is rapidly growing interest in renewable energy source like biomass to be used as an alternative to petroleum. Biomass is biological material from living, or recently living organisms, most often referring to plants or plant-derived materials. Biomass can be converted to higher value products or energy. They include wide range of materials such as: virgin wood from forestry, energy crops specially grown for energy applications, agricultural residues from agriculture harvesting, food waste from food and drink preparation and processing, and post-consumer waste, or industrial waste and co-products from manufacturing and industrial processes [4].

Biomass conversion techniques including thermo-chemical and biochemical conversion are employed for power generation and production of liquid biofuels, chemicals and charcoal, which can be used as activated carbon.

Biochemical conversion makes use of the enzymes of bacteria and other micro-organisms to break down biomass. In most cases micro-organisms are used to perform the conversion process: anaerobic digestion, fermentation and composting.

Thermo-chemical conversion processes use heat or chemicals to convert biomass into another chemical form. Some of the basic techniques are: gasification, combustion, pyrolysis, and gasification. These techniques are separated principally by the extent to which the chemical reactions involved are allowed to proceed. That is mainly controlled by the availability of oxygen and conversion temperature.

Pyrolysis:

Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures in the absence of. It involves the simultaneous change of chemical composition and physical phase, and is irreversible. This process is well recognized as a method for breaking down the complex polymeric constituents of biomass (cellulose, hemicellulose, and lignin) to simpler molecular fragments. The lower molecular weight compounds remain as permanent gases at ambient temperature while the majority of compounds condense to form liquid that is called bio-oil. Before the advent of the petrochemical industry, a number of chemicals such as methanol, phenol, carboxylic acids, and furfural were derived from the pyrolysis liquids generated during charcoal manufacturing. After the global petroleum supply restrictions in the early 1970s, the use of biomass as a source of energy saw renewed interest [5]. The bio-oil can be used as a fuel in diesel engine with modifications in fuel pump, linings, and the injection system. They can be used in oil burners for thermal applications and in combustion boilers to generate electricity or can be blended with standard diesel fuels to form a pollution free green bio-diesel fuel. The bio-oil may have a potential to be used as a chemical feed stocks.

Coconut is a popular plantation and is grown in more than 90 countries worldwide. The world production of coconut sums up to around 55 million tonnes annually [6]. Coconut production plays an important role in India. India accounts for 22.34 per cent of the world's coconut production and is one of the major players in the world's coconut trade. According to figures published in December 2009 by the Food and Agriculture Organization of the United Nations, India is the world's third largest producer of coconuts, producing 10,894,000 tonnes in 2009. [7] Coconut in India is produced in 1894570 ha, and 15729.75 million nuts produced in 2008-2009. [8] The coconut oil; apart from used as edible oil; has varied industrial applications. It is used in the manufacture of toilet soaps, laundry soaps, surface-active agents and detergents, hair tonics, cosmetics, etc. It is used throughout the country as hair oil as it helps growth of the hair. Owing to these qualities coconut oil's market has been getting bigger in the country. At present India produces about 11614 tonnes of coconut oil annually, of which about 50 per cent is absorbed by the toiletry sector (in hair oils, toilet soaps, chemicals for shampoos, etc.), 35 per cent by the households for cooking purposes and 15 per cent is used by confectionery and ice-cream industry. Amount of coconut oil exported to the world market during 2004 was 2.06 million tonnes. [9] The coconut shells generated from oil industry and various uses of coconut need to be utilized properly. Incineration leads to

various environment related problems. These coconut shells will be better utilized if they are pyrolyzed.

Figure 1.1 Coconut shell and powder

It is important to study the nature of bio-oil produced from pyrolysis of coconut shell. So that it can be accessed as fuel.

1.1 Research Objective

In this study, coconut shell has been used as raw materials for pyrolysis process. The different objectives are summarized as:

1. To obtain bio oil from coconut shell by thermal pyrolysis.

2. To characterize the liquid fuel for their physical properties and chemical composition.

3. To characterize the solid residue and prepare activated carbon from it.

4. Kinetic study of thermal pyrolysis for coconut shell.

Chapter 2

Literature Survey

2. Literature survey

2.1 Biomass

Biomass is biological material derived from living, or recently living organisms. In the context of biomass for energy this is often used to mean plant based material, but biomass can equally apply to both animal and vegetable derived material [4]. Biomass is non-fossilized and biodegradable organic material originating from plants, animals and micro-organisms. This includes the products, byproducts, residues and wastes from agriculture, forestry, industrial and municipal wastes. Biomass also includes gases and liquids recovered from the decomposition of non-fossilized and biodegradable organic materials.

2.1.1 Categories of biomass materials

There are five basic categories of material depending upon source and utilities:

- **Virgin wood**, from forestry, arboricultural activities or from wood processing
- **Energy crops**, high yield crops grown specifically for energy applications
- **Agricultural residues**, residues from agriculture harvesting or processing
- **Food waste**, from food and drink manufacture, preparation and processing, and post-consumer waste
- **Industrial waste and co-products**, from manufacturing and industrial processes.

2.1.2 Constituents of biomass

The major constituents of biomass are lignin, cellulose and hemicellulose [10]

2.1.2.1 Lignin

Lignin or lignen is a complex chemical compound most commonly derived from wood, and an integral part of the secondary cell walls of plants[11] and some algae.[12] Lignin is a cross-linked racemic macromolecule with molecular masses in excess of 10,000 u. It is relatively hydrophobic and aromatic in nature. The degree of polymerisation in nature is difficult to measure, since it is fragmented during extraction and the molecule consists of various types of substructures that appear to repeat in a haphazard manner. Different types of lignin have been described depending on the means of isolation [13].

There are three monolignol monomers, methoxylated to various degrees: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [14]. These lignols are incorporated into lignin in the form of the phenylpropanoids p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S), respectively [15].

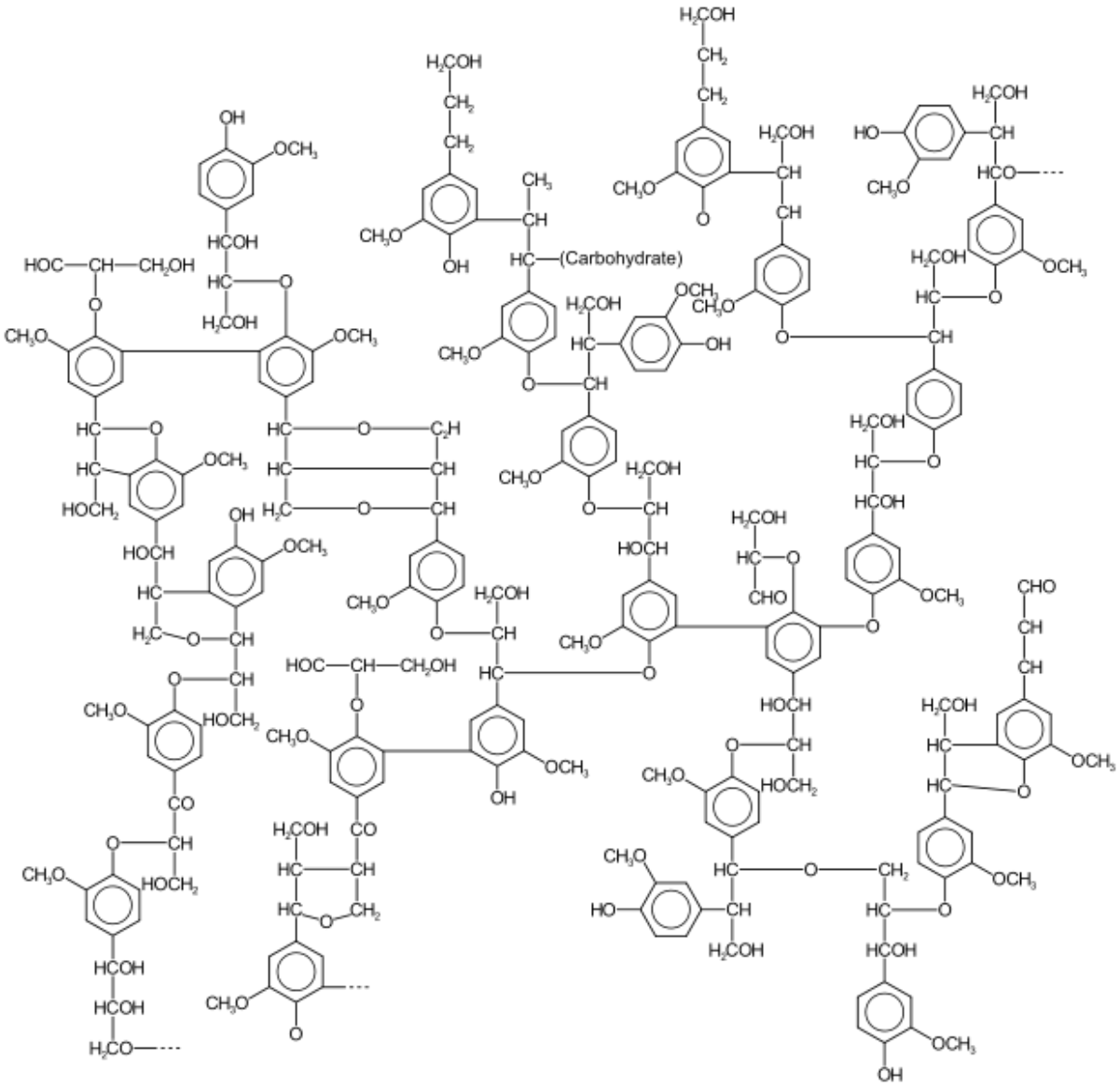

Figure 2.1 lignin structure

2.1.2.2 Cellulose

Cellulose is an organic compound with the formula $(C_6H_{10}O_5)n$, a polysaccharide consisting of a linear chain of several hundred to over ten thousand β(1→4) linked D-glucose units [16][17]. Cellulose is an important structural component of the primary cell wall of green plants, many forms of algae and the oomycetes. Cellulose is the most abundant organic polymer on Earth.

Cellulose has no taste, is odourless, is hydrophilic with the contact angle of 20–30 [18], is insoluble in water and most organic solvents, is chiral and is biodegradable. It can be broken down chemically into its glucose units by treating it with concentrated acids at high temperature.

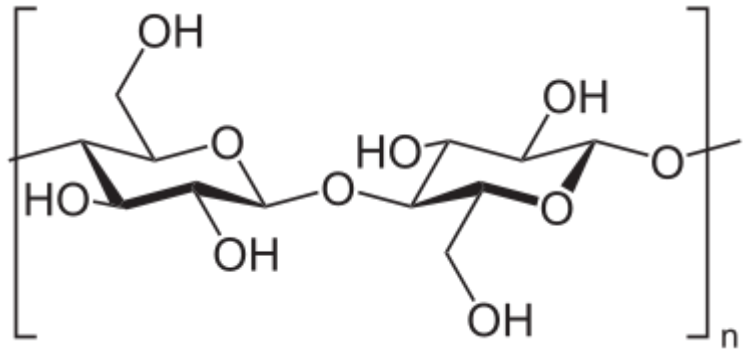

Figure 2.2 Cellulose structure

Cellulose is derived from D-glucose units, which condense through β(1→4)-glycosidic bonds. This linkage motif contrasts with that for α(1→4)-glycosidic bonds present in starch, glycogen, and other carbohydrates. Cellulose is a straight chain polymer: unlike starch, no coiling or branching occurs, and the molecule adopts an extended and rather stiff rod-like conformation, aided by the equatorial conformation of the glucose residues.

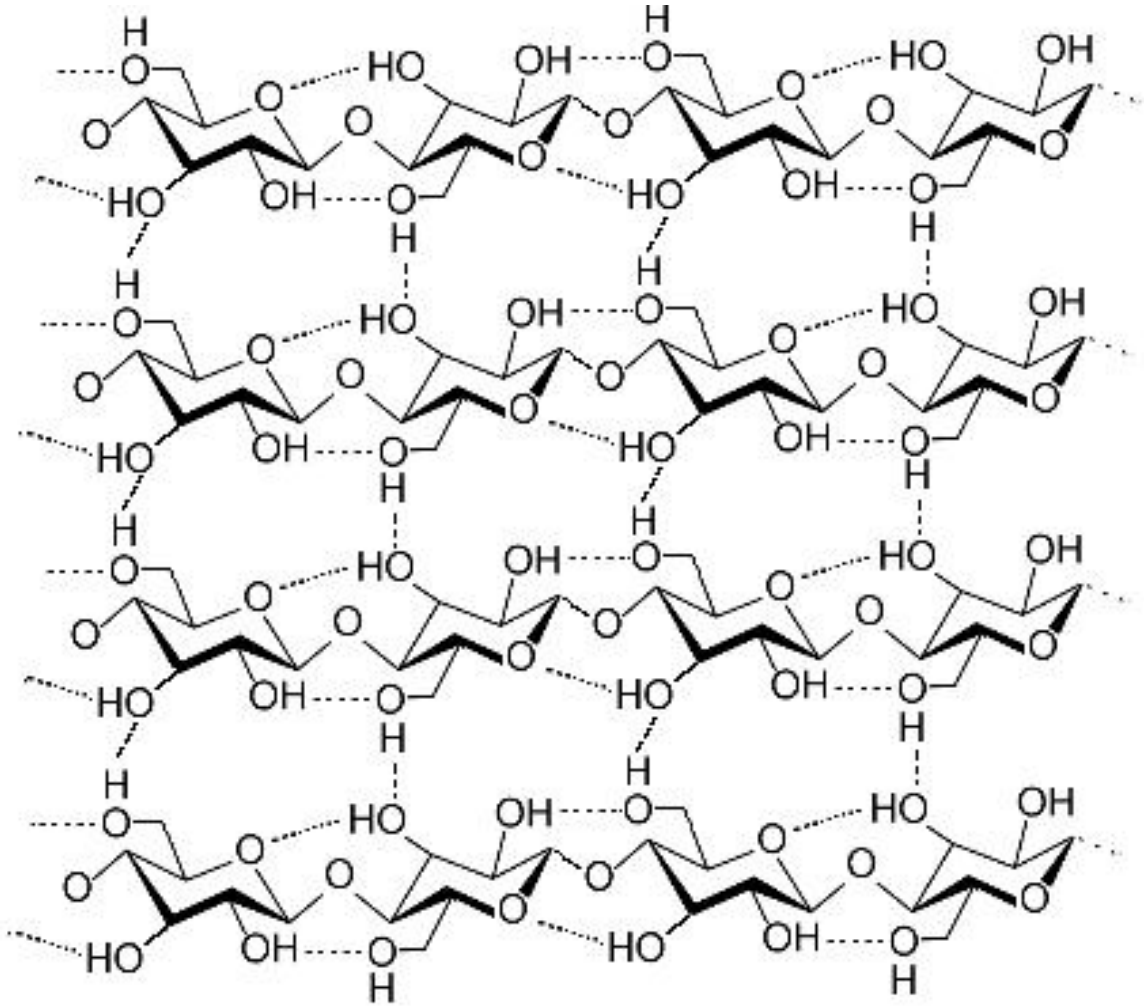

Figure 2.3 A strand of cellulose

The multiple hydroxyl groups on the glucose from one chain form hydrogen bonds with oxygen atoms on the same or on a neighbour chain, holding the chains firmly together side-

by-side and forming microfibrils with high tensile strength. This confers tensile strength in cell walls, where cellulose microfibrils are meshed into a polysaccharide matrix.

2.1.2.3 Hemicellulose

A hemicellulose (Also known as Polyose) is any of several heteropolymers (matrix polysaccharides), such as arabinoxylans, present along with cellulose in almost all plant cell walls. While cellulose is crystalline, strong, and resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength. It is easily hydrolyzed by dilute acid or base as well as myriad hemicellulase enzymes. Hemicelluloses include xylan, glucuronoxylan, arabinoxylan, glucomannan, and xyloglucan. These polysaccharides contain many different sugar monomers. In contrast, cellulose contains only anhydrous glucose. For instance, besides glucose, sugar monomers in hemicellulose can include xylose, mannose, galactose, rhamnose, and arabinose. Hemicelluloses contain most of the D-pentose sugars, and occasionally small amounts of L-sugars as well. Xylose is in most cases the sugar monomer present in the largest amount, although in softwoods mannose can be the most abundant sugar. Not only regular sugars can be found in hemicellulose, but also their acidified form, for instance glucuronic acid and galacturonic acid can be present.

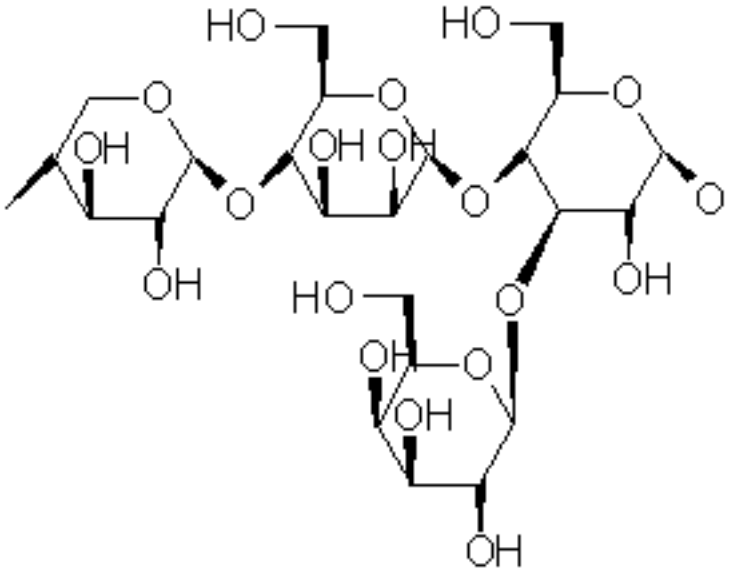

Figure 2.4 structure of hemicellullose

2.2 Methods of conversion of biomass

The following are principal methods of biomass conversion

2.2.1 Biological process

In biological processes, the wet biomass is used as raw materials. The wet biomass is treated with micro-organisms in the presence or absence of oxygen for a longer time. The main

products obtained in this process are bio-ethanol and biogas. Biological processes are of two types, fermentation and anaerobic digestion based on presence or absence of air.

2.2.2 Thermo-chemical process

In these processes, the feed stock is heated in the presence (or absence) of oxygen or water for a short time. The products obtained are fuel gases and bio-oils which can be upgraded by different other processes to get energy reach chemicals of various compositions. The different thermo-chemical processes are combustion, gasification, pyrolysis and hydrothermal liquefaction.

2.2.2.1 Combustion

Combustion or burning is process of conversion of biomass into energy, where the complete oxidation of carbon taking place to CO_2 and the results energy in the form of heat. It is an exothermic chemical reaction between fuel and oxidant. It includes direct burning of dried wood, cow dunk cake, burning of bagasse in boilers and results heat energy.

2.2.2.2 Gasification

Gasification is the conversion, by partial oxidation at high temperature; of a carbonaceous feed stock into a gaseous fuel. The heating value of the resulting gases generally ranges from about one tenth to half that of natural gas, depending on the gasification process used. The product gas can be used in the production of heat, electricity by direct firing in the engine and boiler after suitable clean up.

2.2.2.3 Liquefaction

Liquefaction is a process of conversion of biomass into bio fuel and chemicals where conversion takes place in presence of solvent and catalyst.

2.2.2.4 Alcoholic fermentation

Alcoholic Fermentation, also referred to as ethanol fermentation, is a biological process in which sugars such as glucose, fructose, and sucrose are converted into cellular energy and thereby produces ethanol and carbon dioxide as metabolic waste products. Because yeasts perform this conversion in the absence of oxygen, alcoholic fermentation is considered an anaerobic process. Alcoholic fermentation occurs in the production of alcoholic beverages and ethanol fuel, and in the rising of bread dough.

2.2.2.5 Pyrolysis

Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen. It involves the simultaneous change of chemical composition and

physical phase, and is irreversible. Pyrolysis of biomass produces condensable liquid fraction, non-condensable vapours and solid residue, char.

The process is used heavily in the chemical industry, for example, to produce charcoal, activated carbon, methanol, and other chemicals from wood, to convert ethylene dichloride into vinyl chloride to make PVC, to produce coke from coal, to convert biomass into syngas and biochar, to turn waste into safely disposable substances, and for transforming medium-weight hydrocarbons from oil into lighter ones like gasoline. These specialized uses of pyrolysis may be called various names, such as dry distillation, destructive distillation, or cracking.

In this literature review, biomass pyrolysis for bio fuel or production phenolic compounds is studied. Also, pyrolysis of coconut shell is studied. Pyrolysis of lignin, cellulose and hemicellulose are studied to understand kinetics of pyrolysis of coconut shell.

2.3 Pyrolysis of Coconut shell

Pyrolysis of coconut shell is mainly done to produce char that can be used as activated carbon but very less work is regarding the utilization of the bio-oil produced from coconut shell pyrolysis.

Elisabeth Schröder, Klaus Thomauske, Benjamin Oechsler, Sabrina Herberger, Sabine Baur and Andreas Hornung (2011) produced active carbon from different waste biomass including coconut shell [19]. They generated activated carbon in a two-step process of pyrolysis at 600°C and steam activation at 900 °C. The surface measurements were determined by BET method. Activated carbon from coconut shell char with high BET surface area of around 1000 m^2/g was observed. Coconut shell has been very frequently used precursors to manufacture activated carbon [20][21][22]. Coconut shell has a higher volatile content, which produces granulated carbon with even and large pore volume [23].

K. Prabhakar and R. C. Maheshwari (1986) studied pyrolysis of coconut shell in experimental conditions at different temperatures for varying time periods, to determine the suitable range for obtaining maximum percentage yield of charcoal [24]. They did pyrolysis under field conditions to compare the percentage yield efficiency of charcoal with experimental results. They found the efficiency of pyrolysis in experimental conditions at a temperature of 300°C and 180s time duration is 70%, while infield conditions the efficiency recorded is 27%.

E. Ganapathy Sundaram and E. Natarajan (2009) conducted fixed-bed slow pyrolysis experiments of coconut shell to determine the effect of pyrolysis temperature, heating rate and particle size on the pyrolysis product yields [25]. The effect of vapour residence time on the pyrolysis yield was also investigated by varying the reactor length. Pyrolysis experiments were performed at pyrolysis temperature between 400 and 600°C with a constant heating rate of 60°C/min and particle sizes of 1.18-1.80 mm. The optimum process conditions for maximizing the liquid yield from the coconut shell pyrolysis in a fixed bed reactor were also identified. The highest liquid yield was obtained at a pyrolysis temperature of 550°C, particle size of 1.18-1.80 mm, with a heating rate of 60°C/min in a 200 mm length reactor. The yield of obtained char, liquid and gas was 22-31 wt%, 38-44 wt% and 30-33 wt% respectively at different pyrolysis conditions. The results indicate that the effects of pyrolysis temperature and particle size on the pyrolysis yield are more significant than that of heating rate and residence time. The various characteristics of pyrolysis oil obtained under the optimum conditions for maximum liquid yield were identified on the basis of standard test methods. The pyrolytic oil is found to have HVV of 38.6 MJ/kg.

The conversion of coconut shell into pyrolytic oil by fixed bed fire-tube heating reactor has studied by Joardder Mohammad and Uzzal Hossain (2011) [26]. The major components of the system were fixed bed fire-tube heating reactor, liquid condenser and collectors. The raw and crushed coconut shell in particle form was pyrolized in an electrically heated fixed bed reactor. The products are oil, char and gases. The parameters varied were reactor bed temperature, running time, gas flow rate and feed particle size. The parameters were found to influence the product yields significantly. The maximum liquid yield was 34.3 wt% at 450°C for a feed size of 0.6 mm at a gas flow rate of 6 litre/min with a running time of minute. The pyrolysis oil was obtained at these optimum process conditions were analyzed for physical and chemical properties to be used as an alternative fuel. The oil has HHV of 21.4 MJ/Kg.

2.4 Lignin, Cellulose and Hemicellulose pyrolysis

Since coconut shell like other biomass materials is mainly composed of lignin, cellulose and hemicellulose, it is important to know the pyrolysis characteristics of these compounds. In this part of literature review, the works done regarding the pyrolysis of these compounds is summarized.

The pyrolysis characteristics of three main components (hemicellulose, cellulose and lignin) of biomass were investigated by Haiping Yang, Rong Yan, Hanping Chem, Dong Ho Lee and Chuguang Zheng using a thermo gravimetric analyzer (TGA) with differential scanning

calorimetry (DSC) detector and a pack bed [27]. The releasing of main gas products from biomass pyrolysis in TGA was on-line measured using Fourier transform infrared (FTIR) spectroscopy. In thermal analysis, the pyrolysis of hemicellulose and cellulose occurred quickly, with the weight loss of hemicellulose mainly happened at 220–315 °C and that of cellulose at 315–400 °C. However, lignin was more difficult to decompose, as its weight loss happened in a wide temperature range (from 160 to 900 °C) and the generated solid residue was very high (40 wt.%). From the viewpoint of energy consumption in the course of pyrolysis, cellulose behaved differently from hemicellulose and lignin; the pyrolysis of the former was endothermic while that of the latter was exothermic. The main gas products from pyrolyzing the three components were similar, including CO_2, CO, CH_4 and some organics. The releasing behaviours of H_2 and the total gas yield were measured using Micro-GC when pyrolyzing the three components in a packed bed. It was observed that hemicellulose had higher CO_2 yield, cellulose generated higher CO yield, and lignin owned higher H_2 and CH_4 yield. CO_2 releasing was mainly caused by the primary pyrolysis, while secondary pyrolysis was the main source for releasing of CO and CH_4. Hemicellulose showed higher CO and CO_2 yield, while lignin displayed higher CH_4 releasing. Organics compounds (C=O, C–O–C, etc.) were mainly released out at low temperatures, i.e., 200–400 °C and 300–450 °C from hemicellulose and cellulose, respectively. Nevertheless, almost no organics compound was detected from lignin pyrolysis. The difference might be due to the inherent variance among the chemical structure of the three components, such as hemicellulose appeared more C=O contained organics compounds, while higher contents of OH and C–O was found with cellulos and more methoxyl –O–CH_3 with lignin. In the packed bed, CO_2 and CH_4 mainly evolved out at 400–600 °C, H_2 evolved out at a higher temperature (>400 °C), and the yield of H_2 increased with pyrolysis temperature increasing. It was suggested that different chemical structures of biomass components attribute to different gas product releasing properties. Hemicellulose, with higher carboxyl content, accounted for a higher CO_2 yield. Cellulose displayed a higher CO yield, mainly attributed to the thermal cracking of carbonyl and carboxyl. With a higher presence of aromatic ring and methoxyl, the cracking and deformation of lignin released out much more H_2 and CH_4.biomass components.

Effect of cellulose and lignin content on pyrolysis and combustion characteristics for several types of biomass is tested by Asri Gani, Ichiro Naruse using a thermo-gravimetric analyser [28]. The main compositions of cellulose and lignin contents for several types of biomass are analyzed chemically. Based on the main composition results obtained, the experimental

results for the actual biomass samples are compared with those for the simulated biomass, which is made of the mixture of the cellulose with lignin chemical. The morphological changes before and after the reactions are also observed by a scanning electron microscope. The main compositions in the biomass consisted of cellulose and lignin. The cellulose content was more than lignin for the biomass samples selected in this study. The reaction for the actual biomass samples proceeded with the two stages. The first and second stage corresponded to devolatilization and char combustion during combustion, respectively. The first stage showed rapid mass decrease caused by cellulose decomposition. At the second stage, lignin decomposed for pyrolysis and its char burned for combustion. For the biomass with higher cellulose content, the pyrolysis rate became faster. The biomass with higher lignin content gave slower pyrolysis rate. The cellulose and lignin content in the biomasses was one of the important parameters to evaluate the pyrolysis characteristics. The combustion characteristics for the actual biomass depends on the char morphology produced.

Pyrolysis of cellulose and lignin was studied by T. Haensel , A. Comouth, P. Lorenz, S. I.-U. Ahmed, S. Krischok, N. Zydziak, A. Kauffmann, J.A. Schaefer using X-ray and UV-induced photoelectron spectroscopy (XPS and UPS) and scanning electron microscopy (SEM) [29]. Clean highly oriented pyrolitic graphite (HOPG) was also analysed as a reference material. Asymmetric C1s core level fits and valence band XPS of the samples indicate a graphitic-like structure after the pyrolysis at 1200 °C. Due to the low polar contents in pyrolysed cellulose and lignin, an interaction with methanol under high vacuum conditions could not be identified. From a technical viewpoint a temperature of 1200 °C is attainable without high costs. Therefore, the pyrolysis of wood based polymers containing high amounts of cellulose and lignin are potential low-cost materials for various applications. If it is possible to generate graphite in complex structures made of wood-based polymers, a cheap and energy-efficient method will become available for producing bipolar plates for fuel cells. Technical problems like form instability and foaming are discussed as well as further development and possible modifications of the ground material to achieve optimal compositions.

Chunfei Wua, Zichun Wang, Jun Huang, Paul T. Williams researched into the pyrolysis /gasification of all three main components of biomass, in order to evaluate and compare their hydrogen production and also understand their gasification processes [30]. A fixed bed, two-stage reaction system has been used employing various nickel-based catalysts. Gas concentration (CO, H_2, CO, CO_2 and CH_4) was analysed for the produced non-condensed

gases. Oil by products were analysed by gas chromatography/ mass spectrometry (GC/MS). Various techniques such as X-Ray Diffraction (XRD), scanning electron microscopy (SEM) coupled to an energy dispersive X-ray spectroscopy (EDXS), temperature-programmed oxidation (TPO) were applied to characterize the fresh or reacted catalysts. The experimental results show that the lignin sample generates the highest residue fraction (52.0 wt.%) among the three biomass components. When Ni-Zn-Al (1:1) catalyst was used in the gasification process, gas yield was increased from 62.4 to 68.2 wt.% for cellulose, and from 25.2 to 50.0 wt.% for the pyrolysis/gasification of lignin. Hydrogen production was increased from 7.0 to 18.7 (mmol g1 sample) when the Ni-Zn-Al (1:1) catalyst was introduced in the pyrolysis/gasification of cellulose. Among the investigated catalysts, Ni-Ca-Al (1:1) was found to be the most effective for hydrogen production from cellulose pyrolysis/gasification.

Marion Carrier, Anne Loppinet-Serani, Dominique Denux, Jean-Michel Lasnier, Fre´de´rique Ham-Pichavant, Franc¸ois Cansell, Cyril Aymonier In their work used thermogravimetric analysis as a new method to obtain lignin, hemicellulose and a-cellulose contents in biomass [31]. It is shown that this alternative method lead to comparable results than common methods used for the determination of the a-cellulose content, with an enhancement of the accuracy in the determination of the hemicellulose content. Unfortunately, this method cannot be adopted for the determination of the lignin amount.

2.4.1 Kinetics

Kaushlendra Singh, Dr. Mark Risse, Dr. K. C. Das, Dr. John Worley presented the results of a preliminary investigation of a method using thermo-gravimetric analysis for predicting the fraction of cellulose and lignin in lignin-cellulose mixtures [32]. The concept is based on a newly developed theory of Pyrolytic Unit Thermographs (PUT). The Pyrolytic Unit Thermograph (PUT) is a thermograph showing rate of change of biomass weight with respect to temperature for a unit weight loss. These PUTs were used as input for two predictive mathematical procedures that minimize noise to predict the fractional composition in unknown lignin-cellulose mixtures. The first model used linear correlations between cellulose/lignin content and peak decomposition rate while the second method used a system of linear equations. Results showed that both models predicted the composition of lignin-cellulose mixture within 7 to 18% of measured value. The promising results of this preliminary study will certainly motivate further refinement of this method through advanced research.

2.5 Activated carbon

Activated carbon, also called activated charcoal, activated coal, is a form of carbon processed to be riddled with small, low-volume pores that increase the surface area available for adsorption or chemical reactions.

Since coconut shell pyrolysis also used for preparation of char that used as precursor to activated carbon, in this part, activated carbon is briefly discussed.

2.5.1 Raw materials

For the selection of an appropriate raw material for preparation of porous carbon, several factors are taken into consideration. Industrially, inexpensive material with high carbon and low inorganic (i.e. low ash) content is preferred as raw material for the production of activated carbon. High density of the precursor and sufficient volatile content are of considerable importance. Evolution of volatiles during pyrolysis results in porous char, essential for making activated carbons, while high density contributes to enhanced structural strength of the carbon, essential to withstand excessive particle crumble during use [33].

2.5.2 Carbonisation

During carbonisation, most of the non-carbon elements, hydrogen and oxygen are first removed in gaseous form by pyrolytic decomposition of the starting materials, and the free atoms of elementary carbon are grouped into organised crystallographic formations known as elementary graphite crystallites. Thus carbonisation involves thermal decomposition of carbonaceous material, eliminating non-carbon species producing a fixed carbon mass and rudimentary pore structure. The process is usually carried out at temperature below 800°C in a continuous stream of an inert atmosphere. The important parameters that determine the quality and the yield of the carbonised product are: (i) rate of heating, (ii) final temperature and (iii) soaking time.

2.5.3 Activation

Basically, carbons are described as graphitic or non-graphitic depending upon degree of crystallographic ordering. Graphitic carbons possess three-dimensional symmetry while nongraphitic carbons do not. During carbonisation the free interstices present in the carbon become filled or at least partially blocked by disorganised “amorphous” carbon apparently as a result of deposition of tarry substances. The resulting carbonised product has only a very small adsorption capacity. Presumably, at least for carbonisation at lower temperature, part of the tar remains in the pores between the crystallites and on their surfaces. Such carbonised materials can be then at least partially activated by removing tarry products by heating in

steam or under inert gas or by extraction with a suitable solvent or by chemical reaction. Thus activation is carried out to enlarge the diameters of the pores which are created during the carbonisation process and to create some new porosity thus resulting in the formation of a well-developed and readily accessible pore structure with very large internal surface area. Activation is carried out by two ways as in the following sections.

2.5.3.1 Chemical activation

Chemical activation is carried out with wood as the starting material. In the beginning, wood is impregnated with a concentrated solution of activating agents. It results in degradation of cellulosic material. Chemical-impregnated material is then pyrolysed between 400 and 600°C in the absence of air. Pyrolysed product is cooled and washed to remove activating agent, which is recycled. On calcination, impregnated and chemically dehydrated raw material results in charring and aromatization, and creation of porous structure. Various type of activating agents are used. Some of them are: phosphoric acid, zinc chloride, H_2SO_4;K_2S, KSNS, alkali metal hydroxide, and carbonate and chlorides of Ca^{+2};Mg^{+2} and Fe^{+3}. All activating agents are dehydrating agents which influence the pyrolytic decomposition and inhibit the formation of tar. They also decrease the formation of acetic acid, methanol etc. and enhance the yield of carbon.

2.5.3.2 Physical activation

It is a process by which the carbonised product develops porous structure of molecular dimensions and extended surface area on heat treatment in the temperature range of 800–1000°C in presence of suitable oxidising gases such as steam, CO_2, air.

2.5.4 Classification of activated carbon

Activated carbons are complex products which are difficult to classify on the basis of their behaviour, surface characteristics and preparation methods. However, some broad classification is made for general purpose based on their physical characteristics.

2.5.4.1 Powdered activated carbon

Traditionally, active carbons are made in particular form as powders or fine granules less than 100mm in size with an average diameter between 15 and 25 μm.

2.5.4.2 Granulated activated carbon

Granulated activated carbon have a relatively larger size of particles compared to powdered activated and consequently, present a smaller external surface. Diffusion of the adsorbate is thus an important factor. These carbons are therefore preferred for all adsorption of gases and

vapours as their rate of diffusion are faster. Granulated carbons are used for water treatment, deodorisation and separation of components of flow system.

2.5.4.3 Spherical activated carbon

These are made of small spherical balls wherein pitch is melted in the presence of naphthalene or tetorlin and converted into spheres. These spheres are contacted with solution naphtha, which extracts naphthalene and creates a porous structure. The spheres have high mechanical strength and excellent SO_2 and NO_2 adsorption capacity.

2.5.4.4 Impregnated carbon

Porous carbons containing several types of inorganic impregnant such as iodine, silver, cation such as Al, Mn, Zn, Fe, Li, Ca have also been prepared for specific application in air pollution control especially in museums and galleries.

2.5.4.5 Polymers coated carbon

This is a process by which a porous carbon can be coated with a biocompatible polymer to give a smooth and permeable coat without blocking the pores. The resulting carbon is useful for homoperfusion.

2.6 Bio-oil

Pyrolysis oil sometimes also known as biocrude or bio-oil, is a synthetic fuel under investigation as substitute for petroleum. It is extracted by biomass to liquid technology of destructive distillation from dried biomass in a reactor at temperature of about 500°C with subsequent cooling. Pyrolytic oil (or bio-oil) is a kind of tar and normally contains too high levels of oxygen to be a hydrocarbon. As such it is distinctly different from similar petroleum products.

In pyrolysis of lingo-cellulose material, phenolic compounds have been reported in bio-oil. In this section, some of the works are described that are done to produce phenolic compounds and fractionation of bio-oil.

H. Pakdel and C. Roy (1997) did vacuum pyrolysis of wood bark residues by in a laboratory scale batch reactor [34]. The pyrolysis oil, water, charcoal, and gas were recovered and analysed. The pyrolysis oils were analysed in details for their content in phenolic compounds after derivatization to their acetyl derivatives. The influence of temperature, heating rate, feedstock bed thickness, particle size and feedstock water pre-treatment on the yield of phenols was investigated. The highest yield of phenols was obtained when hardwood bark was soaked in water for 48 hours and pyrolyzed at a temperature of 450°C and a heating rate

of 10°C/min. Pyrolysis performance was evaluated in terms of total phenolic yield and composition.

F. A. Agblevor and S. Besler-Guran (2002) have demonstrated the concept of fractional pyrolysis of biomass. The most important factor is the choice of catalyst [35]. By selecting a suitable catalyst, various components of the biomass feedstocks can be converted in situ into desirable products. In this work we showed that the lignin fraction of the biomass could be effectively converted into phenolics with low char yield when catalysis and pyrolysis reactions were performed simultaneously. Char yields for this process were similar to those obtained from conventional rapid pyrolysis. The molecular mass distribution of fractional catalytic pyrolysis process were about one half that obtained for phenol/neutral fraction in a conventional pyrolysis and there appeared to be considerable demethylation and demethoxylation reactions. The liquid product appeared to be stable with minimal repolymerization reaction.

The review by Dinesh Mohan, Charles U. Pittman, Jr. and Philip H. Steele (2006) focuses on the recent developments in the wood pyrolysis and reports the characteristics of the resulting bio-oils, which are the main products of fast wood pyrolysis [36]. Virtually any form of biomass can be considered for fast pyrolysis. Most work has been performed on wood, because of its consistency and comparability between tests. However, nearly 100 types of biomass have been tested, ranging from agricultural wastes such as straw, olive pits, and nut shells to energy crops such as miscanthus and sorghum. Forestry wastes such as bark and thinnings and other solid wastes, including sewage sludge and leather wastes, have also been studied. In this review, the main (although not exclusive) emphasis has been given to wood. The literature on wood/biomass pyrolysis, both fast and slow, is surveyed and both the physical and chemical aspects of the resulting bio-oils are reviewed. The effect of the wood composition and structure, heating rate, and residence time during pyrolysis on the overall reaction rate and the yield of the volatiles are also discussed. Although very fast and very slow pyrolyses of biomass produce markedly different products, the variety of heating rates, temperatures, residence times, and feedstock varieties found in the literature make generalizations difficult to define, in regard to trying to critically analyze the literature.

Ljudmila Fele Žilnik and Alma Jazbinšek (2012) aimed was to develop a separation process for phenolic fraction recovery from various bio-oils, produced by fast pyrolysis process of

wood and forest residues [37]. Two slightly different schemes were introduced, namely the first one starting with an aqueous extraction of pyrolysis oil and the second one with the simultaneous use of a hydrophobic-polar solvent and antisolvent in the extraction of bio-oil. In both cases the distribution coefficients of phenolic components between the phases as well as extraction factors for major separation stages are presented. Different aqueous solutions were applied and alkali solution was found to be more efficient in comparison to water or aqueous NaHSO3 solution. From various hydrophobic-polar solvents tested, methyl isobutyl ketone (MIBK) was shown to be the most efficient solvent for extraction of phenolics from bio-oil in combination with 0.1 M or 0.5 M aqueous NaOH solution, followed by butyl acetate.

Catalytic microwave pyrolysis of biomass using activated carbon (AC) was investigated by Quan Bu, Hanwu Lei, Shoujie Ren (2012) to determine the effects of pyrolytic conditions on the yields of phenol and phenolics [38]. Bio-oils with high concentrations of phenol (38.9%) and phenolics (66.9%) were obtained. These levels were higher than those obtained by pyrolysis without AC addition and were closely related to the decomposition of lignin. A high concentration of esters (42.2% in the upgraded bio-oil) was obtained in the presence of Zn powder as catalyst and formic acid/ethanol as reaction medium. Most of the esters identified by GC–MS were long chain fatty acid esters. The high content of phenols and esters obtained in this study can be used as partial replacement of petroleum fuels after separation of oxygenates or as feedstock for organic syntheses in the chemical industry after purification.

Chapter 3

Materials

And Methods

3. Materials and Methods

3.1. Collection and Preparation of Raw materials

Coconut shells have been collected from nearest temples and are powdered before pyrolysis.

3.1.1. Coconut shell powder preparation

Before putting coconut shells for co-pyrolysis, they are processed to be reduced to fine particles. The process is as follows. Coconut shells are dried in sun, and then hand crushed to large size pieces which are then dried in oven at 105°C for removal of moisture. The dried coconut shell pieces are then sent to ball mill for further grinding. Before putting coconut shell pieces, the inside of ball mill is washed with water and wiped with wet cloth and left for drying. Initially they are processed at large ball mill to reduce them to medium size pieces of around 1 cm^2. Rotating speed of 50 rpm is used. The product is then processed to small-size ball mill where they are ground again. The finer product is separated using sieve shaker, BSS 52. Thus final particle size of ground coconut shell is less than 1 mm.

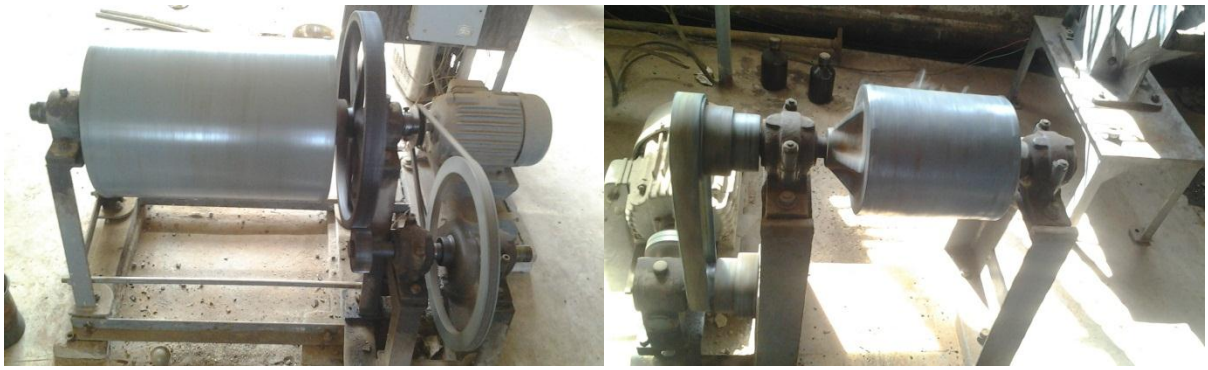

Figure 3.1 Big and small Ball Mill

3.2 Characterization of raw material

3.2.1 Proximate Analysis

It provides information on moisture content, ash content, volatile matter content and fixed carbon content of the material. Fixed carbon other than ash does not vaporize when heated in the absence of air. Fixed carbon is usually determined by subtracting the sum of the first three values that is moisture, ash, and volatile matter (weight percent from 100 percent).So, it is very important for economic reasons to know the moisture and ash contents of the material. They do not contribute to the heating value of a coal. In most cases ash is an undesirable residue also a source of pollution. In some purposes (use as a chemical feedstock, liquefaction) the presence of mineral matter may be needed. Mostly heat value of the material comes from after excluding moisture, volatile matter, and fixed carbon content.

3.2.2. Ultimate Analysis

Ultimate analysis is performed to determine the elemental composition of the material. Ultimate analyses are used to determine the carbon, hydrogen, nitrogen, sulfur, ash, oxygen contents of the material. For the specific applications, other chemical analyses can be employed. These include identifying the forms of sulfur present. Sulfur occurs in the form of sulfide minerals, sulfate minerals, or organically bound sulfur. Other specific cases the analyses may involve determining the trace elements present which influence the suitability of the material for a particular purpose. This may include methods for reducing environmental pollution and so forth.

It was carried out using a CHNSO elemental analyzer (Variael CUBE Germany) which provides carbon, hydrogen, nitrogen, sulphur percentage composition. And when sum of theses compositions is subtracted from 100, it gives oxygen percentage composition.

3.2.3 Thermo-Gravimetric Analysis

Thermo gravimetric analysis or thermal gravimetric analysis is mainly considered as a type of testing on samples which determines changes in weight to a temperature program in a controlled atmosphere. It relies on a high degree of precision in two basic aspects which is weight and temperature. As most weight loss curves look more or less similar, the weight loss curve may require keen analysis before results may be interpreted. A derivative weight loss curve can identify the point where weight loss is most prominent. Interpretation is limited without further modifications of the overlapping peaks. For the determination of the composition and purity one must take the mass of the substance in the mixture by using thermal gravimetric analysis.

Thermal gravimetric analysis is a process which involves heating a mixture to a high enough temperature so that one of the components decomposes into a gas that dissociates into the air.

Thermo gravimetric analysis is a process which utilizes heat and stoichiometry ratios to determine the percent by mass ratio of a substance. If the compounds in the material remain known, then the percentage by mass is determined by taking the weight of what is left in the mixture and dividing it by the initial mass. After knowing the mass of the original mixture, the total mass of impurities liberating upon heating then the stoichiometric ratio can be used to calculate the percent mass of the substance in a sample. TGA is used in research and testing to determine characteristics of materials such as absorbed moisture content of materials, the level of Inorganic and organic components in materials, polymers, to

determine degradation temperatures, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

The analyzer consists of a high-precision balance with a pan of platinum loaded with the sample. Pan resides in a furnace and is heated or cooled during the experiment. Different process using a quartz crystal microbalance is devised for measuring smaller samples on the order of a microgram versus milligram with conventional TGA. Sample is placed in a small electrically heated oven with a thermocouple for accurate measurement of the temperature. The atmosphere may be supplied with an inert gas to prevent oxidation or other undesired reactions. A computer is employed to control the instrument.

Pyrolysis is heating of a substance in absence of air at a particular temperature. Therefore, the temperature for effective pyrolysis of the coconut shell powder has to be determined. For this purpose, thermo-gravimetric analysis (TGA) of the sample was done using a DTG60 instrument. Around 20-30 milligrams of sample was taken and heated up to a final temperature of 600°C and a residence time of 1 minute at 600°C was allowed. TGA were performed at a heating rate of 10°C/Min and 20°C/Min. Thermo-gravimetric weight loss curve was plotted against temperature. It provides a range of temperature in which maximum thermal degradation of coconut shell powder takes place.

3.3. Experimental set up

The pyrolysis setup used in this experiment is shown in Figure 3.2.

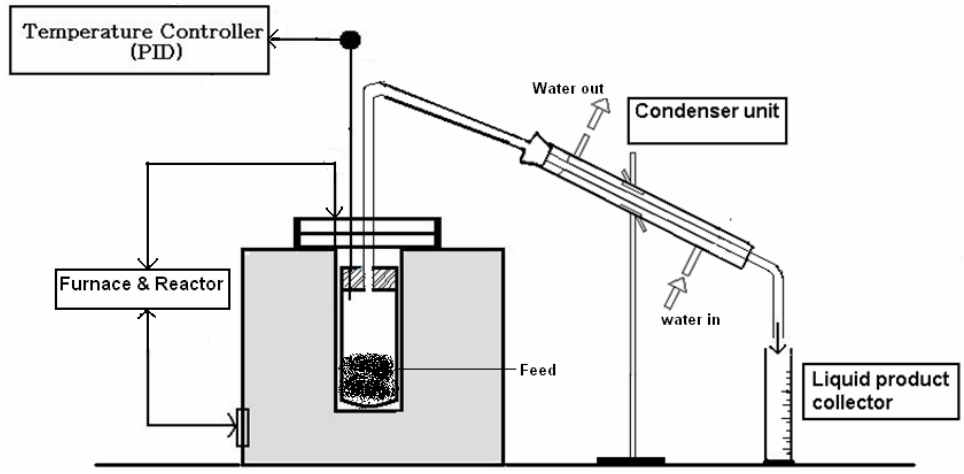

Figure 3.2 Pyrolysis experimental set up

It consists of a semi batch reactor made of stainless steel tube (length- 145 mm, internal diameter- 37 mm and outer diameter- 41 mm) sealed at one end and an outlet tube at other end. The reactor is heated externally by an electric furnace, with the temperature being

measured by a Cr-Al: K type thermocouple fixed inside the reactor, and temperature is controlled by an external PID controller. A certain amount of waste plastics and coconut shell sample are loaded in pyrolysis reaction. The condensable liquid product is collected through the condenser and weighed. After pyrolysis, the solid residue left inside the reactor is weighed. The weight of gaseous / volatile product was calculated from the material balance.

3.4. Sample Pyrolysis Runs

Once the temperature range was established then sample pyrolysis runs were done with 15gms of coconut shell powder in that range at intervals of 25°C to determine the temperature at which maximum yield of liquid product is obtained. It was heated externally by electric furnace at a heating rate of 20°C min^{-1} .The temperature of the furnace is maintained by a highly sensitive proportional-integral-derivative(PID) controller and the temperature is measured by Cr-Al:K type thermocouple fixed in the reactor. During sample runs various data like yield of char, and yield of liquid product were noted down. Variation in yield of char, liquid product and gas (volatiles) with respect to temperature is plotted.

3.5 Characterization of liquid product

3.5.1 Physical Characterization of Bio-Oil

Physical properties such as density, specific gravity, viscosity, conradson carbon, flash point, fire point, pour point, cloud point, calorific value and sulphur content of the bio-oil are determined using the standard methods.

3.5.2 Chemical Characterization of Bio-Oil

3.5.2.1 FTIR

Fourier Transform Infrared spectroscopy (FTIR) is an important analysis technique that detects various characteristic functional groups available in oil. Interaction of an infrared light with oil the chemical bond will stretch, contract, and absorb infrared radiation in a specific wave length range in the presence of the rest of molecules. Based on this, the principle functional groups present in the pyrolytic oil were identified. The FTIR spectra were collected generally in the range of 400-4000 cm^{-1} region with 8cm^{-1} resolution. Absorption in the infrared region makes changes in vibrational and rotational status of the molecules. The absorption frequency depends greatly on the vibrational frequency of the molecules. The absorption intensity depends on how the infrared photon energy can be transferred to the molecule. This depends on the change in the dipole moment that occurs as a result of molecular vibration. A molecule will absorb infrared light only if the absorption

causes a change in the dipole moment. All compounds except for elemental diatomic gases such as N_2, H_2 and O_2, have infrared spectra and most components present in a flue gas is also analysed by their characteristic infrared absorption. If only one species is analysed, a species-specific instrument can also be used. Analysis is carried out in a narrow wavelength interval, where the species of interest has a characteristic absorption. Other components present in the sample also absorb at the analytical wavelength, so the spectrometer should be calibrated for cross sensitivities. Quantification of several components absorbing in the mid infrared region (400- 5000cm^{-1}), either conventional dispersive infrared analysis or Fourier Transform Infrared (FTIR) spectroscopy can also be used. Compared to dispersive IR analysis, FTIR analysis is faster and has a better signal to noise ratio.

In a FTIR instrument, the monochromator and the slits are replaced by an interferometer of Michelson type. A beam of radiation is divided into two beams by means of a beam splitter. A path difference between the beams is also introduced whereupon it is allowed to recombine. In this way, interference between the beams is obtained. Intensity of the output beam from the interferometer is monitored as a function of path difference using an appropriate detector.

In order to determine the functional groups present in the pyrolytic oil, Fourier Transform Infrared spectroscopy of the oil is being analyzed in a Perkin-Elmer infrared spectrometer.

3.5.2.2 GC-MS

Gas Chromatography – Mass Spectrometry of the pyrolytic oil is being performed using a GC-MS OP 2010 [SHIMADZU] analyzer to determine the Chemical compounds present in the oil. Chromatography is specially used to separate mixtures of chemicals into individual components for identification. After isolation, the components can be evaluated individually. In all most all chromatography, separation generally occurs when the sample mixture is introduced or injected into a mobile phase. In case of liquid chromatography, the mobile phase is a solvent. In the gas chromatography (GC), the mobile phase is an inert gas for example helium. Mobile phase carries the sample mixture through what is referred as stationary phase. The stationary phase is considered as a chemical that can also attract components in a sample mixture. This tube is called as a column. Columns can be glass or stainless steel of various dimensions. The mixture of compounds in the mobile phase interacts with the stationary phase. Each and every compound in a mixture interacts at a different rate. That interact the fastest will exit (elute from) the column first. Those that interact slowest will exit the column last. By observing the changing characteristics of the mobile phase and the

stationary phase the different mixtures of chemicals can be separated. Further refinements to this separation process are also made by changing the temperature of the stationary phase or the pressure of the mobile phase. GC has a long, thin column containing a thin interior coating of a solid stationary phase (5% phenyl-, 95% dimethyl siloxane polymer). This 0.25 mm diameter column is called as a capillary column. This particular column is used for semi volatile, non-polar organic compounds such as the PAHs we will look at. The capillary column is held in an oven that can be programmed to increase the temperature gradually (or in GC terms, ramped). As the temperature increases, that compounds which have low boiling points elute from the column sooner than those that have higher boiling points. There are actually two distinct temperature, separating forces and stationary phase interactions mentioned previously. After the compounds are separated, they just elute from the column and enter a detector. Detector is capable of creating an electronic signal whenever the presence of a compound is detected. Greater the concentration in the sample the bigger the signal becomes. The signal is then processed by the computer. Time from when the injection is made (time zero) to when elution occurs is referred to as the retention time (RT). While the instrument runs, the computer generally generates a graph from the signal. Each of the peaks in the chromatogram represents the signal created only when a compound elutes from the GC column into the detector. The x-axis shows the RT, and the y-axis shows the intensity (abundance) of the signal.

3.5.2.3 1H- NMR:

Proton NMR also known as Hydrogen-1 NMR, or 1H NMR is the application of nuclear magnetic resonance in NMR spectroscopy with respect to hydrogen-1 nuclei within the molecules of a substance. To determine the structure of its molecules in samples where natural hydrogen (H) is used, practically all of the hydrogen consists of the isotope 1H (hydrogen-1 is having a proton for a nucleus). A full 1H atom is called protium. NMR spectra are recorded in the solution and solvent protons must not be allowed to interfere. Deuterated (deuterium = 2H, often symbolized as D) solvents especially for use in NMR are preferred, such as deuterated chloroform ($CDCl_3$). However, a solvent without hydrogen such as carbon tetrachloride (CCl_4) or carbon disulphide (CS_2) may also be used. Deuterated solvents were usually supplied with a small amount of (typically 0.1 %) of tetramethylsilane (TMS) as an internal standard for calibrating the chemical shifts of each analyte proton. TMS is generally a tetrahedral molecule, with all the protons being chemically equivalent which gives one single signal, used to define a chemical shift = 0 ppm. It is volatile, making sample recovery easy as well. Modern spectrometers are also able to reference spectra based on the residual

proton in the solvent (e.g. the $CHCl_3$, 0.01 % in 99.99 % $CDCl_3$). Deuterated solvents are now commonly supplied without TMS. Deuterated solvents permit the use of deuterium frequency-field lock (also known as deuterium lock or field lock) to offset the effect of the natural drift of the NMR's magnetic field B_0. In order to provide the deuterium lock, the NMR monitors the deuterium signal resonance frequency from the solvent and makes changes to the B0 to keep the resonance frequency constant. Additionally, the deuterium signal is used to accurately define 0 ppm as the resonant frequency of the lock solvent. The difference between the lock solvent and 0 ppm (TMS) are well known. Proton NMR spectra of the most organic compounds are characterized by chemical shifts in the range +14 to - 4 ppm and by spin-spin coupling between protons. The integration curve for each of the proton reflects the abundance of the individual protons.

1H-NMR spectra were recorded by using a 400 MHz, BRUKER DPX-400, High performance digital FT–NMR spectrometer by using chloroform-d containing TMS (tetramethylsilane) as the internal standard.

3.6 Characterization of char

3.6.1 Proximate and ultimate analysis of the pyrolytic char

The proximate analysis was done by ASTM D3173-75. And the ultimate analysis was done by using Elemental CHNS analyzer.

3.6.2 SEM analysis

The char product derived from the coconut shell pyrolysis was characterized by Scanning Electron Microscope (Model: JEOL-JSM-6480LV SEM) with an acceleration voltage of 15 kV at different magnification values to have a clear view on pore density and diameter.

3.6.3 BET Surface area analysis

BET surface analysis is physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material. Higher the surface area better is the adsorption behavior of the adsorbent.

3.6.4 Powder XRD analysis

Solid samples were characterized by powder X-ray diffraction (XRD) using a Hiltonbrooks X-ray powder diffraction set consisting of a Hiltonbrooks 3 kW generator model DG3 (30 kV, 20 mA), detector control module and step motor drive module. It was equipped with a Philips PW 1050 goniometer and a proportional detector. The X-ray generator consists of a Seifert copper long fine focus X-ray tube for Cu Kα radiation at 1.5406 Å, a Sietronics

curved graphite monochromatic, and a Ni filter to absorb Cu Kβ radiation. It helps us to understand the crystalline or powdered characteristics of the material.

XRD scan was done for 2θ range of 5° to 65° with 2θ of 3° per minutes.

3.7 Preparation of activated carbon

Preparation of activated carbon is by following steps

i. The dried coconut shell powder transfer into the pyrolytic reactor and reactor put inside the furnaces, by maintaining 575°C temperature.
ii. After pre-carbonized of material, the material is crushed into powder or granular form using hand blender.
iii. Carbonaceous material was sized with the help of sieving technique and the30 BSS (British Standard Scale) sieve was used for 500 micron size as particle size.
iv. Resulting sample was washed with distilled water and unwanted materials get separated as waste filtrate.
v. Properly washed carbonized carbon is impregnated with 40% diluted H_2SO_4 acid solution with an impregnated ratio (W/W) of 4:1 for nearly 10 hours.
vi. Resulting chemically acid washed Carbon is again washed with single distilled water.
vii. Finally the washed Activated Carbon is kept in the oven at 110°C for 3 hours for removal of moisture
viii. Dried activated adsorbent kept in plastic storage bottle container for further use.

3.8 Characterisation of activated carbon

The proximate analysis and ultimate analysis were done. The SEM was done to determine surface morphology. BET surface area analysis gave the active surface area. XRD was also done. These details about these methods are described before.

Chapter 4

Results

And Discussion

4. Results and Discussion

4.1. Proximate and Ultimate analysis of Coconut shell

The Proximate Analysis result of coconut shell powder determines the distribution of its contents. This shows coconut shell has good amount volatile content to be used as a material for pyrolysis.

Sl. No	Properties	% w/w
1	Moisture content	10.1
2	Volatile matter	64.6
3	Fixed carbon	11.2
4	Ash content	14.2

Table 4-1 Proximate analysis of coconut shell

The Ultimate analysis of Coconut shell powder is as follows.

Sl. No.	Element	percentage
1	Carbon	64.23
2	Hydrogen	4.89
3	Nitrogen	4.77
4	Sulpher	3.50
5	Oxygen	22.61

Table 4-2 Ultimate analysis of coconut shell

The empirical formula of the coconut shell is $C_{5.35}H_{4.85}N_{0.34}S_{0.11}O_{1.41.}$ The theoretical calorific value is 22.43 MJ/Kg.

4.2. Thermo Gravimetric Analysis

TGA (Thermo Gravimetric Analysis) study helps us in determining the range of temperature of pyrolysis. A sharp bend in the curve shows the temperature at which the pyrolysis has to be started and the temperature at which the curve gets flat shows the end temperature of the pyrolysis. From figure 4.1 and figure 4.3, the range of pyrolysis was observed to be from 250 to 550°C at 10°C/min and 250 to more than 600°C at 20 °C/min. In this case the first stage decomposition represents the evaporation of moisture contents; Second decomposition indicates the formation of volatiles. During the Third stage, the pyrolysis residue slowly decomposed, with the weight loss velocity becoming smaller and smaller and the residue ratio tends to be constant at the end the decomposition of hydrocarbon.

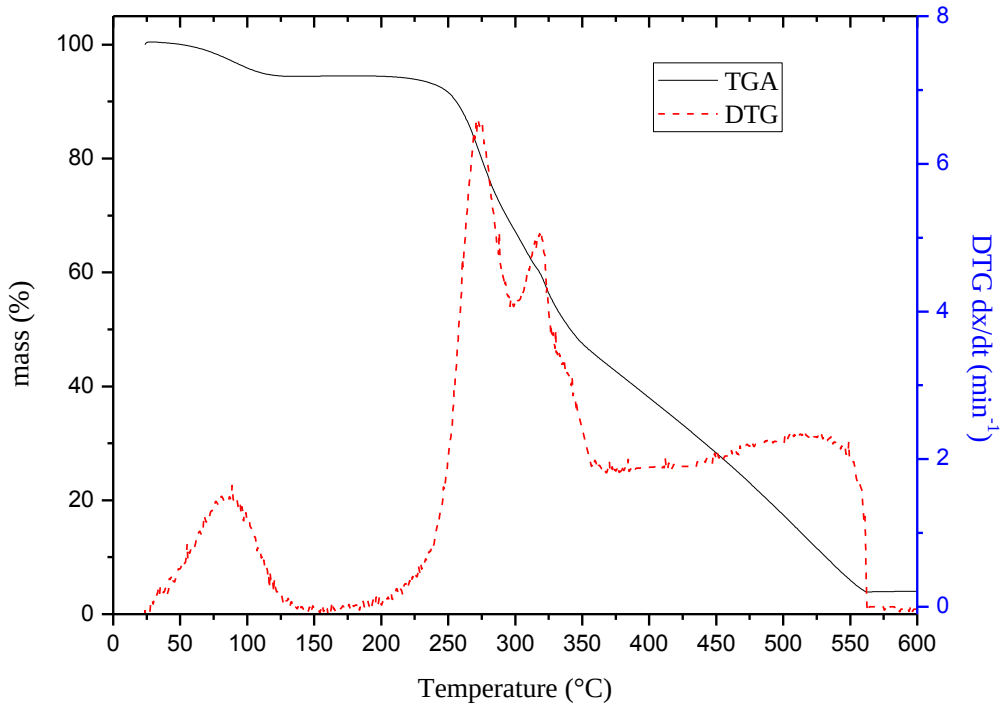

Figure 4.1 TGA and DTG for 10 °C/min heating rate

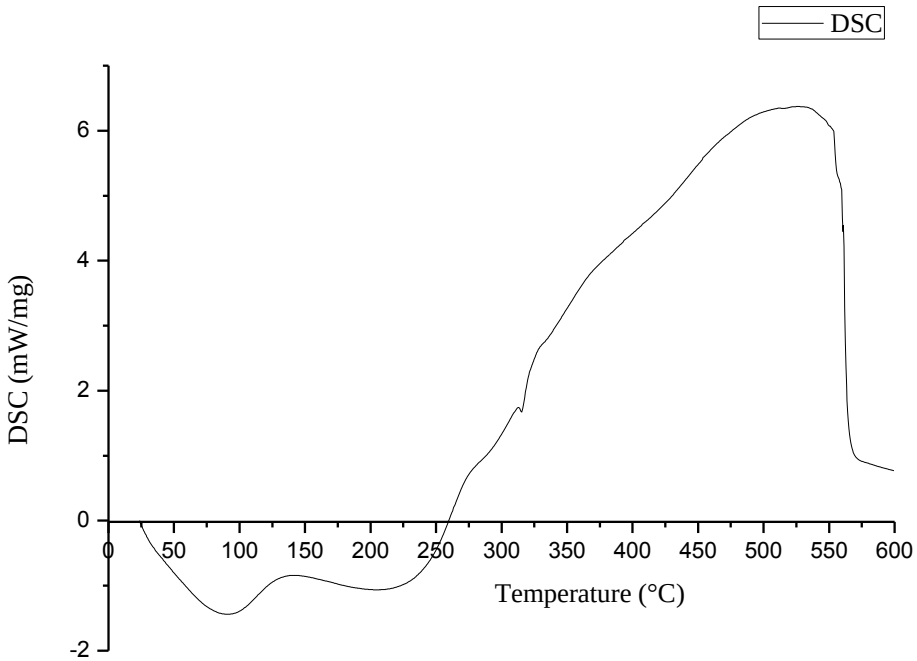

Figure 4.2 DSC for 10 °C /min heating rate

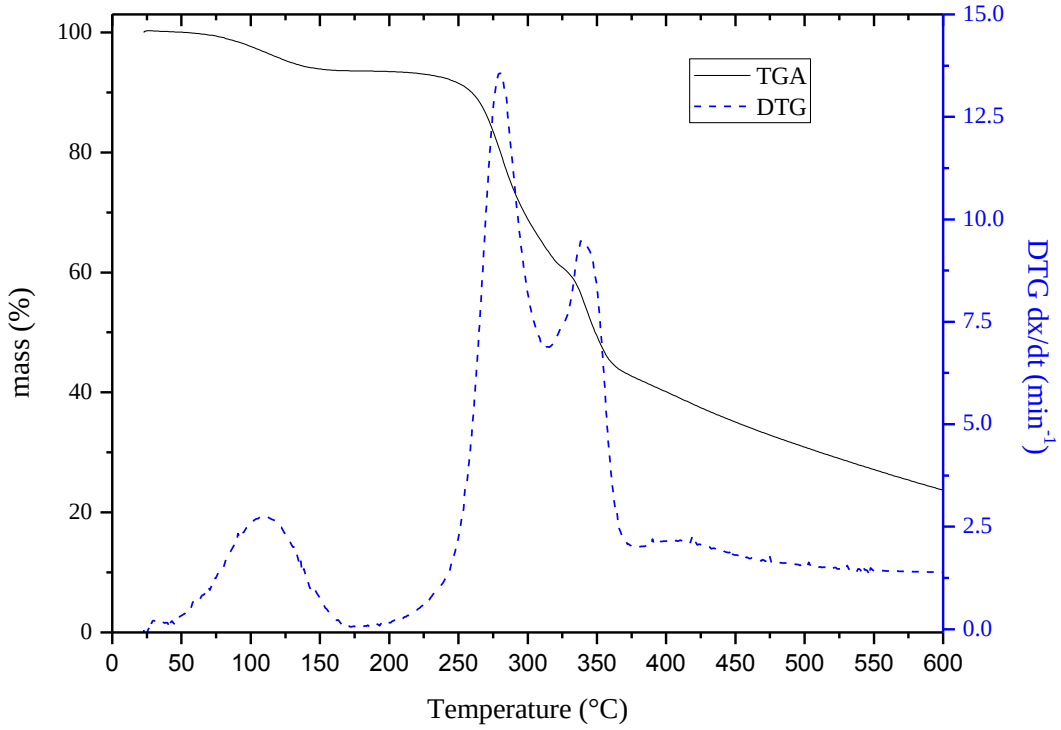

Figure 4.3 TGA and DTG for 20 °C /min heating rate

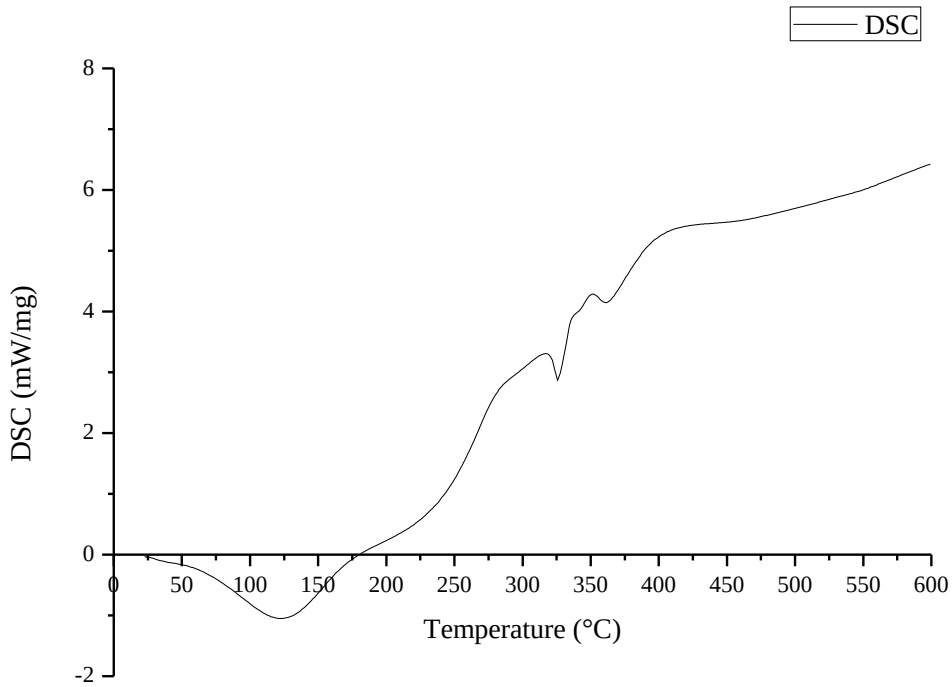

Figure 4.4 DSC for 20 °C /min heating rate

Due to high decomposition rate per unit time, the rapid decomposition zone or Second stage of decomposition is treated as active pyrolytic zone. During this stage, the intermolecular associations and weaker chemical bonds are destroyed.

Coconut shell usually contains 32% of hemicellulose, 14% cellulose, and 46% lignin. Pyrolysis decomposed these compounds. Hemicellulose will decompose at temperature 200- 260 °C, cellulose in 240-350 °C, and lignin between temperature 300 and 500 °C [32]. The DSC curve shows the parts with endothermic and exothermic reactions. Near 100 °C, endothermic reaction is observed because heat is supplied for the removal of moisture.

4.3. Experimental Results:

Materials are processed and the experiments are done to generate data regarding yield at different temperatures.

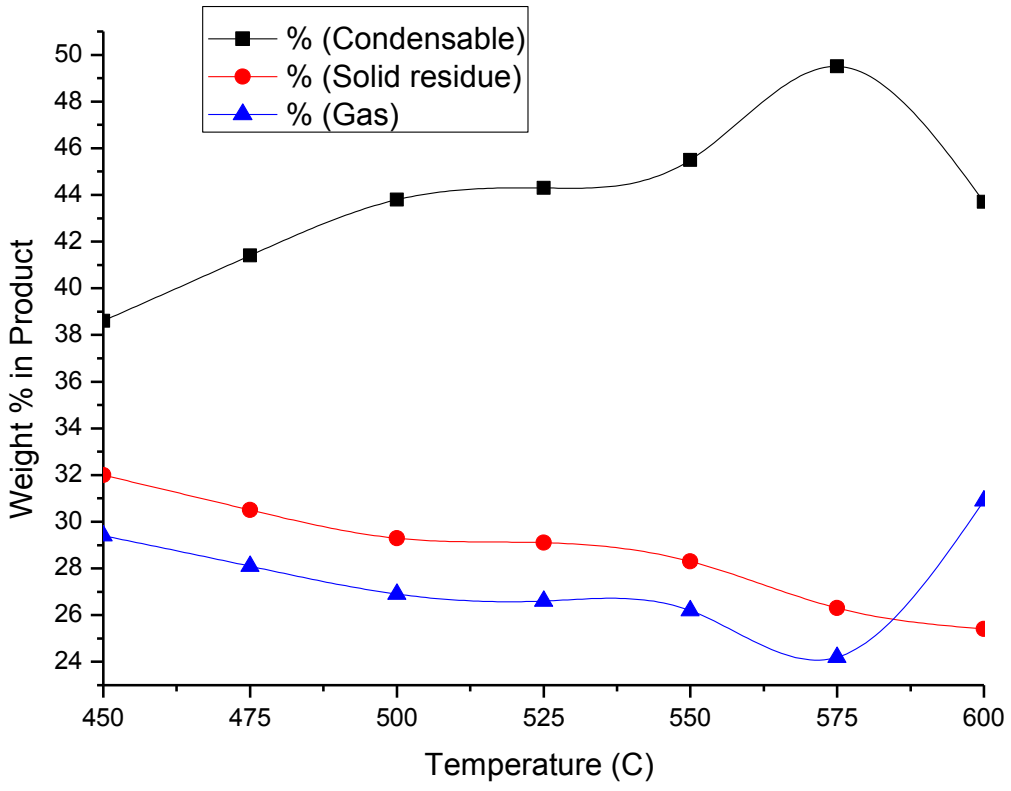

Figure 4.5 Variation of weight % of products with Temperature

Table 4-3 presents the product distribution from pyrolysis of coconut shell for a pyrolysis temperature of 450 - 600 °C. The liquid increased from 38.6 to maximum 49.5 wt% at 575°C

and decreased afterwards. The gas yield decreased from 29% to a minimum of 24% at 575 °C and then increased afterwards. The solid yield decreased continuously from 32% at 450 °C.

The decrease in gas yield at lower temperature is due to incomplete decomposition of the shell (pyrolysis is not complete). Decrease in liquid and char yield and increase in gas yield at higher temperature are due to not only the secondary cracking of pyrolysis vapour but also solid char.

Temp (°C)	Condensable fraction	Carbonaceous residue	Gas/Volatiles
450	38.6	32.0	29.4
475	41.4	30.5	28.1
500	43.8	29.3	26.9
525	44.3	29.1	26.6
550	45.5	28.3	26.2
575	49.5	26.3	24.2
600	43.7	25.4	30.9

Table 4-3 Experimental results regarding yield

Similar results were observed in the fixed – bed slow pyrolysis of rapeseed at 30°C/min in which the liquid yield increased from 41 to 47 wt% when the pyrolysis temperature increased from 400°C to 550 °C (Ozlem and Kocker, 2004), but the liquid yield of safflower seed press cake and soybean cake were found to be 30 to 33 wt% and 26 to 30 wt% respectively at the same temperature range (Sensoz and Angin, 2008); Putin et al. (2002) [25]. This similarity and variation of the liquid yield could be due to the variation of the components present with individual biomass.

4.4 Physical Characterization of Bio-Oil

Various physical properties determined are presented in tabular form as below.

Sl. No.	Properties	Results obtained	Test Method
1	Specific Gravity @ 15°C/15°C	1.0740	IS:1448 P:16
2	Density @ 15°C g/cc	1.0536	IS:1448 P:16
3	Kinematic Viscosity @ 40°C in cst	1.47	IS:1448 P:25
4	Conradson Carbon Residue	5.56%	IS:1448 P:122
5	Flash Point	44°C	IS:1448 P:21
6	Fire Point	52°C	IS:1448 P:20

7	Pour Point	minus 15°C	IS:1448 P:10
8	Gross Calorific Value in MJ/Kg	19.75	IS:1448 P:6
9	Sulphur Content	02.34%	IS:1448 P:33

Table 4-4 Physical properties of bio-oil

4.5 Chemical Characterization of Bio-Oil

The chemical characterisation of bio-oil includes FTIR, GC-MS, and 1HNMR analysis. Ultimate analysis also has been done.

4.4.1 FTIR of oil sample

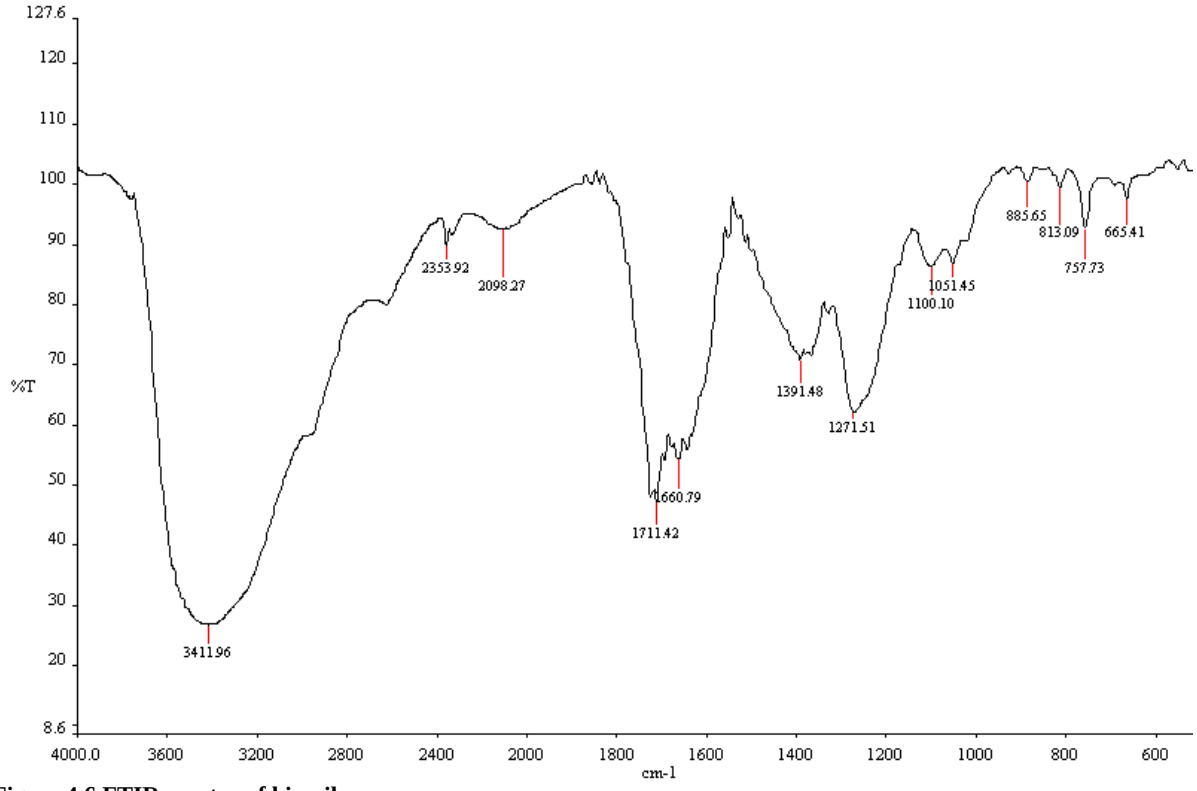

Figure 4.6 FTIR spectra of bio-oil

Fourier Transform Infrared spectroscopy (FTIR) is an important analysis technique which detects various characteristic functional groups present in oil. On interaction of an infrared light with oil, chemical bond will stretch, contract, and absorb infrared radiation in a specific wave length range regardless structure of the rest of the molecules. Figure 16 shows the FTIR spectra of coconut shell oil. The different assignments of the FTIR spectra of coconut shell oil are summarized in table 5 which shows the presence of mostly alkane and alkenes. The results were found consistent when compared with the results of GCMS.

Wave number (cm $^{-1}$)	Type of vibration	Functional group
3411.96	H–bonded O–H stretch (Broad strong band)	Alcohol/Phenol
2353.92	Doublet	Carbon dioxide
2098.27	C≡C stretch (medium)	Terminal alkyne
1711.42	C=O stretch (strong)	Ketone or Carboxylic acid
1660.79	C=C stretch (medium)	Alkene
1391.48	C=C stretch (medium)	Aromatic
1271.51	C–O stretch	Alcohol
1100.10	C–O stretch	Ether
1051.45	C–O stretch	Ether
885.65	C–H bend	Aromatic
813.09	C–H bend	Aromatic
757.73	C–H bend	Aromatic
665.41	C–H bend	Aromatic

Table 4-5 Peaks and functional groups from FTIR

4.4.2 GC-MS of oil sample

The GC-MS analysis of the oil sample obtained from coconut shell was carried out to know the exact composition of the oil (Figure 4.8) and 28 compounds were detected which are summarized in the Table 4-6.

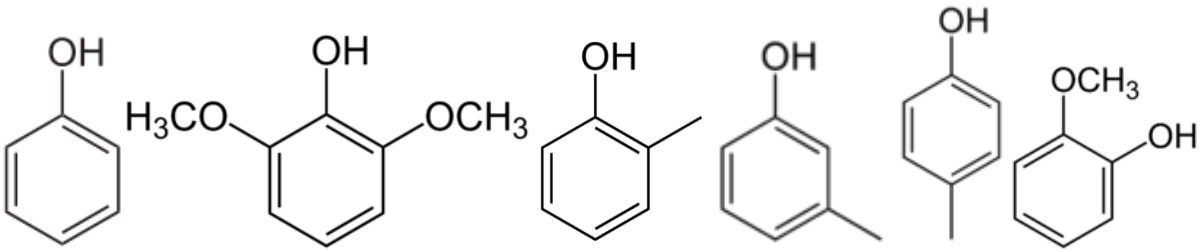

Figure 4.7 Some of the important products formed: Phenol, Syringol, o-,m-,p-Cresol, Guaiacol

With phenol being present in highest amount (28.5%), many derivatives of phenol were also detected. Phenol is mostly converted to chemicals used as precursor to plastics. For example, bisphenol-A is a precursor to polycarbonates and epoxide resins used for paints and coatings etc. Cyclohexane can be derived from phenol via partial hydrogenation is a precursor to nylon. Non-ionic detergents are produced by alkylation of phenol to give alkylphenols. Phenol is used in production of caprolactam which go in to end uses such as textiles, carpets packaging etc. Phenol is also used for manufacturing of drugs like aspirin, phenacetin etc.

Around 95% of current world production of phenol is by oxidation of 1-methylbenzene. Currently phenolic resins are being made from pyrolysis oil produced from biomass.

Guaicol contributes to flavour of many compounds. In preparation of food by smoking, Guiacol is the main chemical responsible for smoky taste, whereas syringol is responsible for smoke aroma. Vanillic acid is used as a flavouring agent. Cresols are used to dissolve other chemicals, also used as disinfectants and deodorizers.

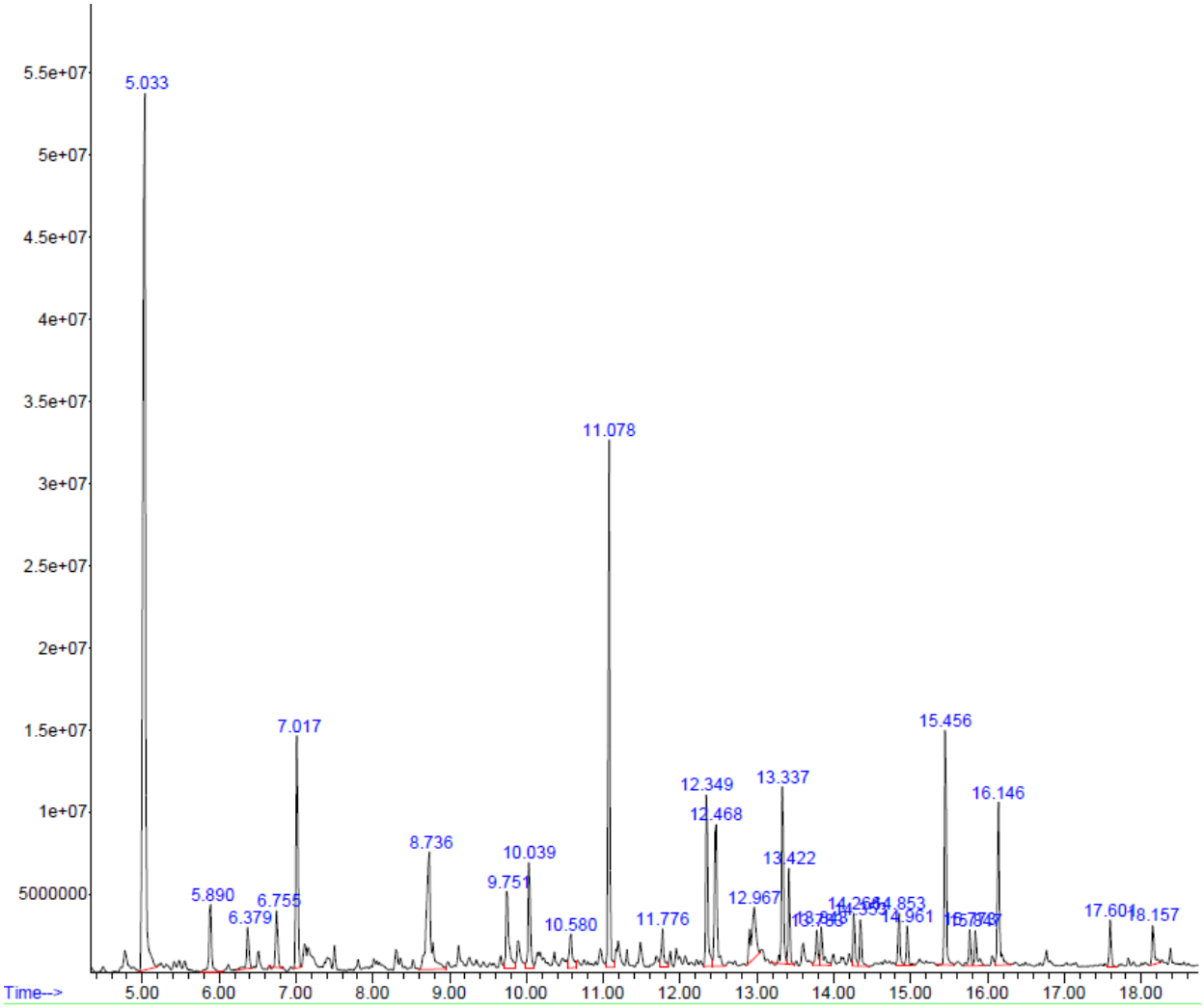

Figure 4.8 GCMS chromatogram of bio-oil

Peak	Retention time	Area %	Compound Name	Molecular Formula
1	5.033	28.52	Phenol	C_6H_6O
2	5.890	2.08	3-methyl-1,2-Cyclopentanedione	$C_6H_8O_2$
3	6.384	1.15	2-methyl-Phenol	C_7H_8O

4	6.761	1.44	p-Cresol	C_7H_8O
5	7.023	5.36	2-methoxy-Phenol	$C_7H_8O_2$
6	8.736	6.15	Creosol	C_7H_8O
7	9.753	2.79	3-methoxy-1,2-Benzenediol	$C_7H_8O_3$
8	10.043	2.91	4-ethyl-2-methoxy- Phenol	$C_9H_{12}O_2$
9	10.581	1.33	2-Methoxy-4-vinylphenol	$C_9H_{10}O_2$
10	11.075	10.09	2,6-dimethoxy- Phenol	$C_8H_{10}O_3$
11	11.772	1.11	Vanillin	$C_8H_8O_3$
12	12.353	4.36	4-hydroxy-3-methoxy-Benzoic acid	$C_8H_8O_4$
13	12.469	4.58	Methylparaben	$C_8H_8O_3$
14	12.963	2.87	D-Allose	$C_6H_{12}O_6$
15	13.340	4.22	1-(2,6-dihydroxy-4-metho xyphenyl)-Ethanone,	$C_9H_{10}O_4$
16	13.427	1.90	1-methyl-N-vanillyl- (+-)-2-Phenethanamine,	$C_{18}H_{23}NO_6$
17	13.790	0.82	Dodecanoic acid	$C_{12}H_{24}O_2$
18	13.848	1.23	2,3,5,6-Tetrafluoroanisole	$C_7H_4F_4O$
19	14.270	1.32	2,6-dimethoxy-4-(2-propenyl)-Phenol	$C_{11}H_{14}O_3$
20	14.357	1.13	2,4'-Dihydroxyacetophenone oxime	C_8H_9NO
21	14.851	1.25	N-(4-Methoxyphenyl)-2-hydroxyimino-acetamide	$C_9H_{10}N_2O_3$
22	14.967	0.89	4-hydroxy-3,5-dimethoxy-Benzaldehyde	$C_9H_{10}O_4$
23	15.461	4.68	2,6-dimethoxy-4-(2-propenyl)-Phenol	$C_{11}H_{14}O_3$
24	15.078	0.85	1-(4-hydroxy-3,5-dimethoxyphenyl)-Ethanone	$C_{10}H_{12}O_4$
25	15.853	1.04	4-Hydroxy-2-methoxycinnamaldehyde	$C_{10}H_{10}O_3$
26	16.143	3.85	1-(2,4,6-trihydroxy-3-methylphenyl)-1-Butanone	$C_{11}H_{14}O_4$
27	17.595	1.01	Pentadecanenitrile	$C_{15}H_{29}N$
28	18.162	1.08	n-Hexadecanoic acid	$C_{16}H_{32}O_2$

Table 4-6 various compounds in bio-oil identified using GCMS

4.4.3 NMR of oil sample

^{1}H- NMR spectra were recorded by using a 400 MHz, Bruker DPX-400, High performance digital FT–NMR spectrometer was done by using chloroform-d containing TMS (tetramethylsilane) as the internal standard.

^{1}H-NMR band assignments corresponding to structural features of coconut shell pyrolytic oil is given in Table 4-9. CH_3 CH_2 and CH hydrogen attached to an aromatic ring were present in higher proportion in bio-oil and that accounts to 23.93 %. About 19.09% of hydrogen was attached to aromatic ring. Phenolic (OH) or olefinic protons account for 12.65% of hydrogen. CH_2 and CHβ to an aromatic ring (naphthenic) were present in 19.49% and CH_3 γ or further from an aromatic ring were also present.

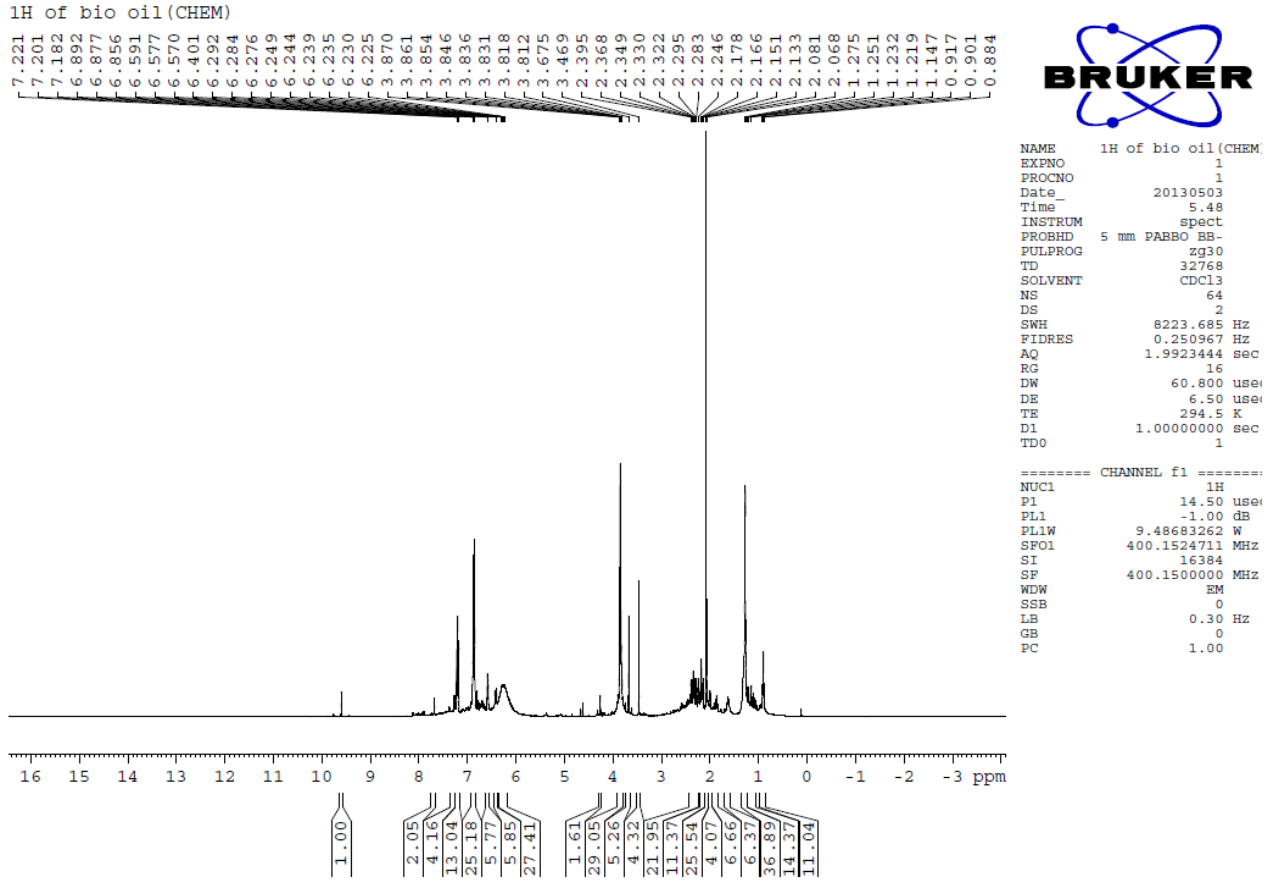

Figure 4.9 1HNMR spectrum for bio-oil

Type of hydrogen	Chemical shift (ppm)	Percentage of Total Hydrogen (%)
Aldehyde	10.5-9.5	0.38
Aromatic	8.5-6.5	19.09
Phenolic (OH) or olefinic proton	6.5– 5.0	12.65

Hydroxyl groups or ring-join methylene (Ar–CH_2–Ar)	4.5– 3.3	15.30
CH_3 CH_2 and CH to an aromatic ring	3.3– 2.0	23.93
CH_2 and CH β to an aromatic ring (naphthenic)	2.0– 1.6	04.96
β-CH_3, CH_2 and CH γ to an aromatic ring	1.6– 1.0	19.49
CH_3 γ or further from an aromatic ring	1.0– 0.5	04.20

Table 4-7 1HNMR result for the bio-oil

4.4.4 Ultimate Analysis

Table 4-8 shows the elemental composition of coconut shell pyrolytic oil and compared with diesel. From the analysis it can be observed that the carbon percentage of coconut shell Pyrolytic oil is less than that of diesel oil. The empirical formula is $C_{4.93}H_{3.44}N_{0.3}S_{0.07}O_{1.93.}$ The bio-oil has more sulphur and oxygen content than desired.

Element	**coconut shell Pyrolytic oil**	**Diesel**
Carbon	59.14	85.72
Hydrogen	03.47	13.2
Nitrogen	04.21	0.18
Sulpher	02.34	0.3
Oxygen	30.84	0.6
Empirical formula	$C_{4.93}H_{3.44}N_{0.3}S_{0.07}O_{1.93}$	$C_{7.14}H_{13.09}N_{0.01}S_{0.01}O_{0.04}$

Table 4-8 ultimate analysis of pyrolytic oil

The calorific value is 19.75 MJ/kg.

4.5 Characterisation of Char

4.5.1 Proximate and Ultimate analysis

Proximate and ultimate analysis of coconut shell char was done to determine the presence of volatile matter and characterized for its elemental composition by CHNS analysis and are tabulated in Table 4-10. Its Empirical formula was also determined. It was found that even after pyrolysis still some negligible amount of volatile matter was present in the char. Its higher fixed carbon content leads to preparation of activated carbon.

Sl. No	**Property**	Percent (%)
1	Moisture content	3.73
2	Volatile content	5.52
3	Ash content	19.65
4	Fixed carbon	71.55
5	C	75.5

6	H	5.15
7	N	4.14
8	S	0.15
9	O	15.06
13	Empirical formula	$C_{6.29}H_{5.11}N_{0.01}S_{0.004}O_{0.63}$

Table 4-9 Proximate and ultimate analysis of bio-oil

4.5.2 SEM Analysis of char

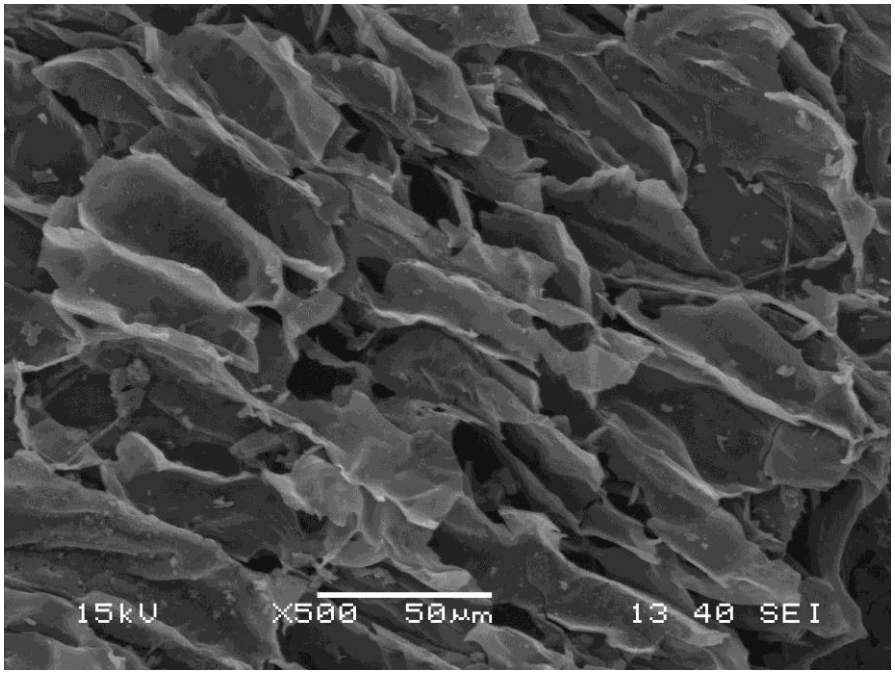

Figure 4.10 SEM image of coconut shell char at 500X magnification

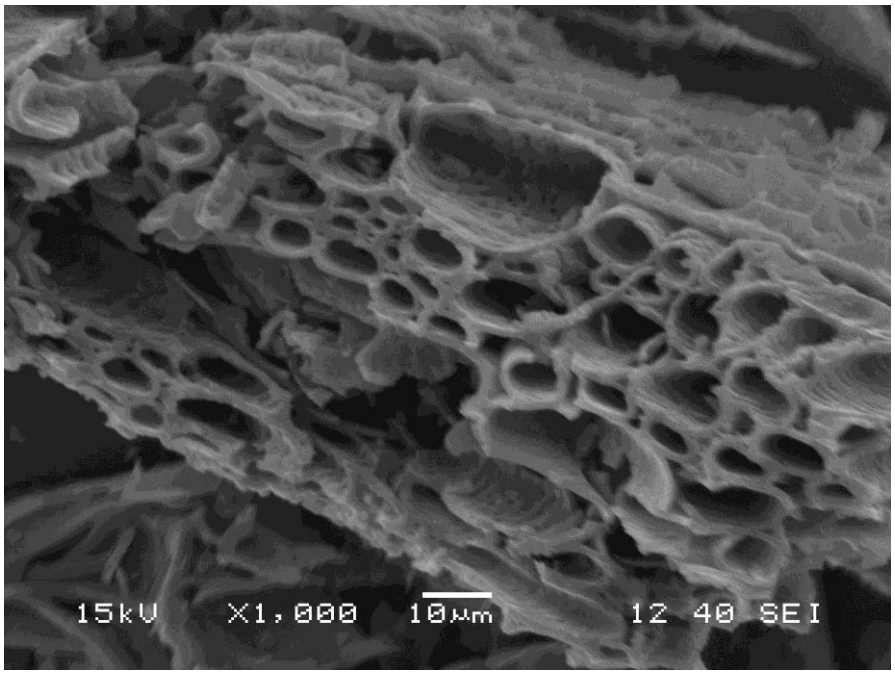

Figure 4.11 SEM image of coconut shell char at 1000X magnification

SEM analysis was done to find the surface morphology of char. Figure 4.9 and 4.10 are SEM of coconut shell char taken at 500X and 1000X magnification. These images showed heterogeneous distribution of pores and rough texture. Presence of micropores and mesopores detected.

4.5.3 XRD analysis of raw material and char

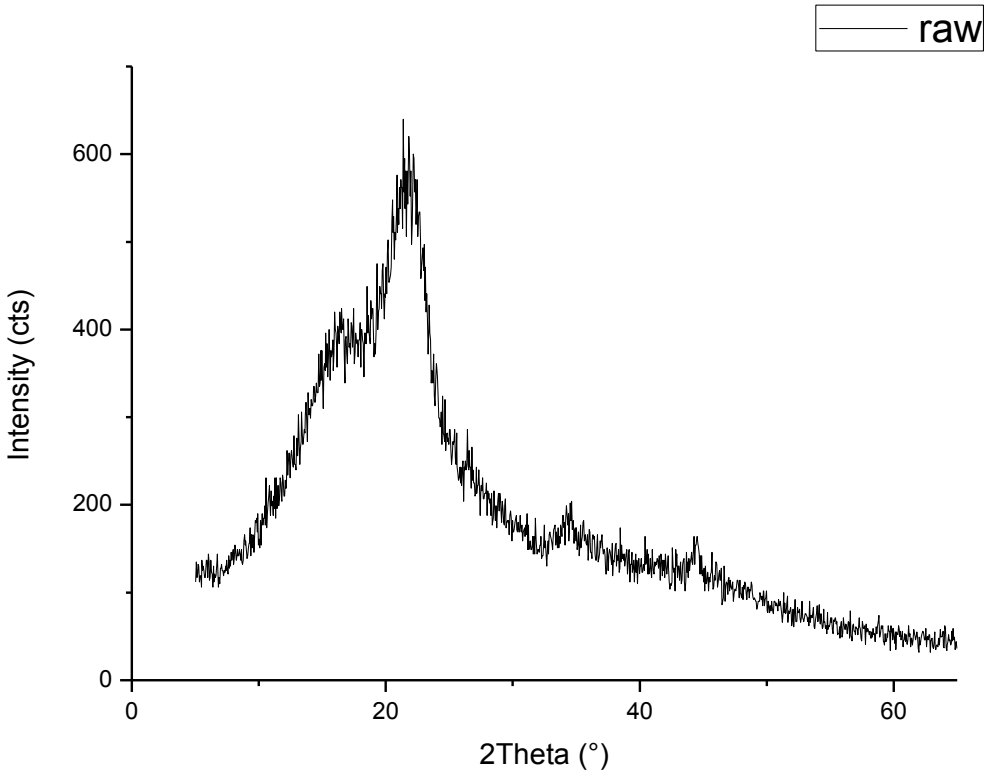

Figure 4.12 XRD analysis of coconut shell powder

The X-ray diffraction patterns of raw material i.e. coconut shell powder and the solid residue formed by its pyrolysis are given in Figs. 4.12 and 4.13. As seen in Fig. 4.12, the patterns of coconut shell exhibit well defined peaks (2θ) at 12.34°, 16.28°, 20.86°, 26.42°, 34.38°, 43.43°, 44.43°, 45.64°, 45.97° and 46.63°. Out of these, 12.34°, 16.28°, 20.86°, 26.42° and 34.38° are mainly of the crystal of cellulose (JCPDS No. 03-0223) and the remaining amorphous areas are due to lignin and hemicelluloses component in coconut shell.

The effect of chemical modification of lignocellulosic materials on their crystallinity has been investigated by various researchers. When the crystal content is high then one may observe some new peaks or peak position at around 15.1° divided into two peaks, but when the fibre contains high amounts of amorphous material such as lignin, hemicellulose, and amorphous cellulose, these two peaks are smeared, thus appearing as one broad peak (Fig.4.12).

From Fig. 4.13 it is observed that there are some new peaks (2θ) of various intensities in the amorphous region 40–65°. The diffraction patterns of coconut shell char exhibits four prominent peaks at 35.2°, 56.6°, 59.8° and 62.3°.

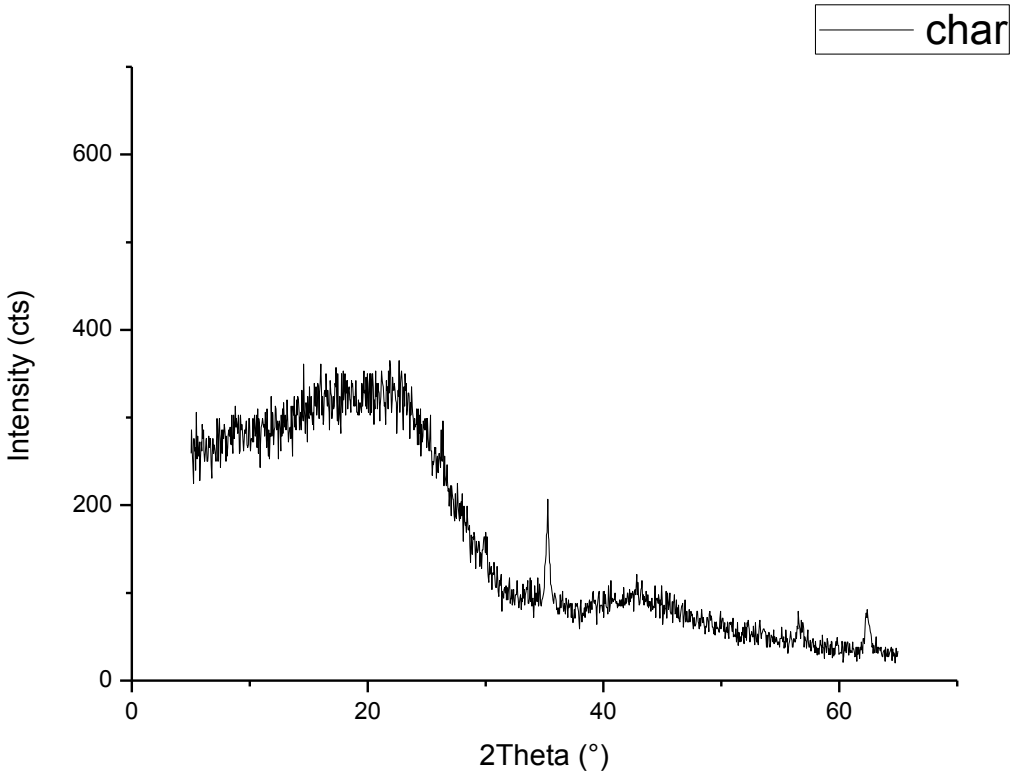

Figure 4.13 XRD analysis of coconut shell char

4.5.4 BET surface area Analysis

BET surface area analysis gave an active area of 515 m^2/gm.

4.6 Characterisation of activated carbon

4.6.1 Proximate and Ultimate analysis

Sl.No	**Property**	Percent (%)
1	Moisture content	1.84
2	Volatile content	2.62
3	Ash content	8.65
4	Fixed carbon	86.7
5	C	82.5
6	H	3.14

7	N	4.15
8	S	0.15
9	O	10.06
13	Empirical formula	$C_{6.87}H_{3.12}N_{0.01}S_{0.004}O_{0.63}$

Table 4-10 Proximate and ultimate analysis of active carbon

4.6.2 SEM Analysis of activated carbon

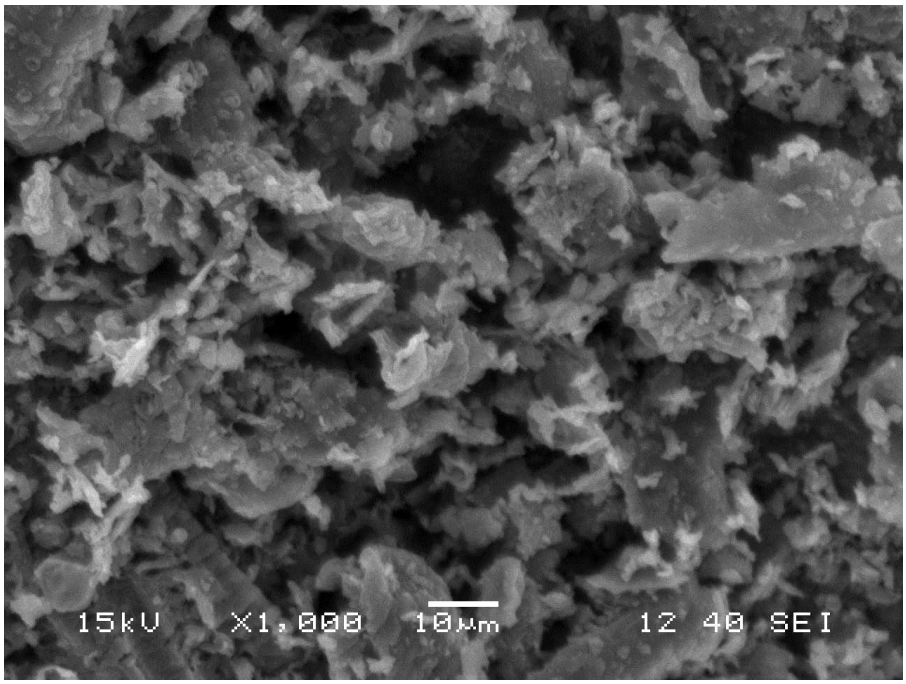

Figure 4.14 SEM image of activated carbon at 1000X magnification

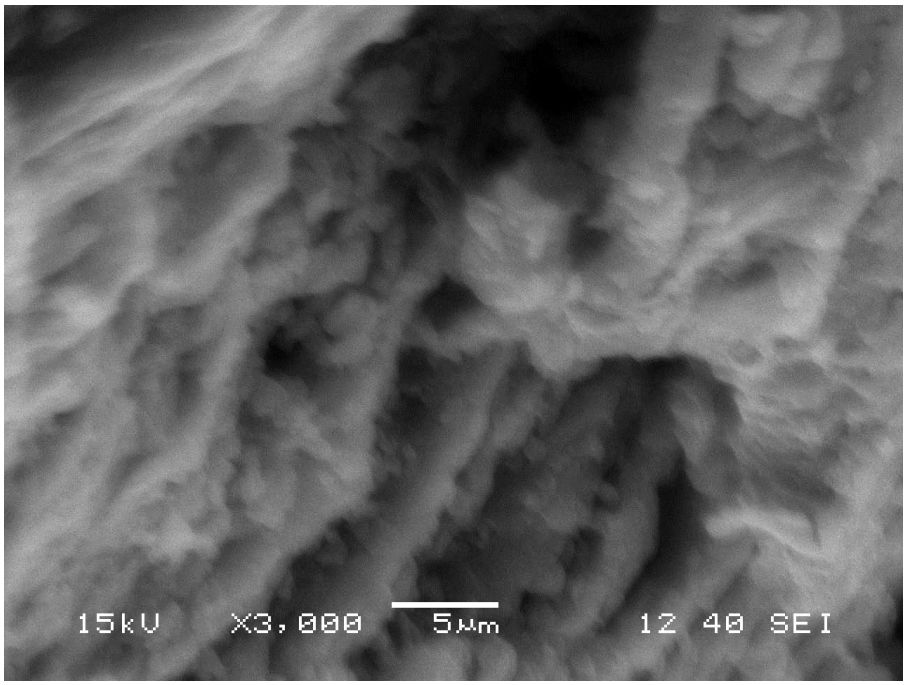

Figure 4.15 SEM image of activated carbon at 3000X magnification

The SEM analysis showed the surface morphology. Figure 4.14 and 4.15 are taken at 1000X and 3000X magnification respectively.

4.5.3 XRD analysis of activated carbon

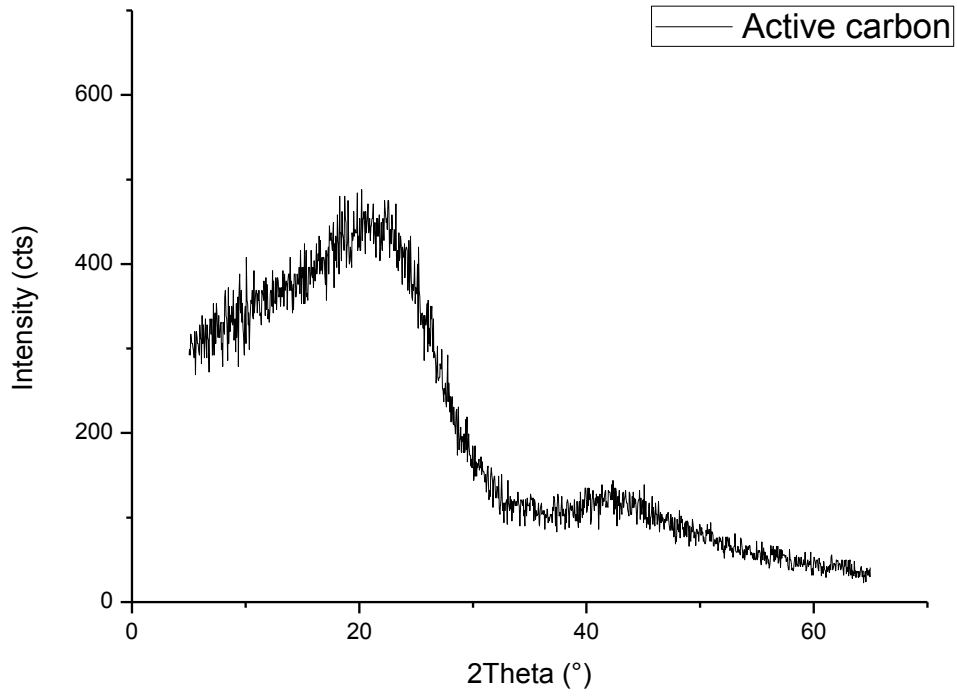

Figure 4.16 XRD analysis of active carbon

Compared to char, peaks at 2θ of 35.2° and 62.3° are absent in this active carbon due to degradation.

4.5.4 BET surface area Analysis

BET surface area analysis gave an active area of 780 m^2/gm. Thus activation enlarged the diameters of the pores and created some new porosity thus resulting in the formation of a well-developed and readily accessible pore structure with very large internal surface area.

Chapter 5

Kinetic study

5. Kinetic Study

5.1 Introduction

Thermal behaviour of coconut shell can be improved by knowing thermal degradation kinetics. So the kinetic study of coconut shell powder pyrolysis provides a useful basis upon which to design a pyrolysis reactor. A thermo gravimetric analysis (TGA) technique is an excellent way for studying the kinetics of thermal degradation. It provides information on pre-exponential factor and activation energy. The mechanisms of pyrolysis include a wide range of different reactions. Not every reaction causes the release of a volatile molecule. Some only cause a change in mechanical properties. During thermo gravimetric analysis, only the weight loss is measured on heating, that means only those reactions causing the weight loss are considered.

5.2 Mechanism and Calculation of Kinetic Parameters

TGA is used to find out the kinetic parameters in addition to the decomposition of coconut shell comprises a large number of reactions in parallel and series, whereas TGA measures the overall kinetics rather than individual reactions. However, it is useful in providing comparative kinetic data under different reaction conditions such as temperature and rate of heating. In this work first-order decomposition reaction with integral method was used to evaluate the kinetic parameters. The first order reaction with respect to the amount of undecomposed material states that A (Solids) → B (Solid) + C (Volatile)

For 1st order reaction, we have:

$$\frac{dX}{dt} = K(1 - x)$$

$$K = K_0 * e^{(-\frac{E_a}{RT})}$$

The extent of conversion or fraction of material pyrolyzed, X was defined by expression

$$X = \frac{W_0 - W_t}{W_0 - W_\infty}$$

Where W_0 is the initial weight (mg), W_t is the weight after "t" minutes (mg), and W_∞ is the weight after pyrolysis (mg).

R = Universal gas constant, 8.314J $K^{-1}mol^{-1}$

K_0= Pre-exponential factor (min^{-1}), and

E_a= Activation energy (KJ mol^{-1}) with linear heating rate of, A in K min^{-1}

$$A = \frac{dT}{dt}$$

Integrating results in

$$\ln[-\ln(1-X)] = \ln\left[\left(\frac{K_0 RT^2}{AE_a}\right)\left(1-\frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT}$$

Since it may be shown that for most values of E and for the temperature range of the pyrolysis, the expression $\ln[K_0RT^2/AE_a(1-2RT/E_a)]$ in above equation is essentially constant, if the left side of the equation is plotted versus 1/T, a straight line may be obtained if the process can be assumed as a first order reaction. From the slope, −E/R, the activation energy E can be determined, and by taking the temperature at which $W_t = (W_0 + W_f)/2$ in the place of T in the intercept term of equation 4, the pre-exponential factor A can also be determined. Fig 5.1 shows the kinetic Plots of ln[-ln(1-X)] against 1/T of coconut shell at heating rate of 20°C/min and should correspond to a straight line with a slope of $(-E_a/R)$ giving the activation energy. And the pre-exponential factor also can be calculated by using activation energy and the intercept.

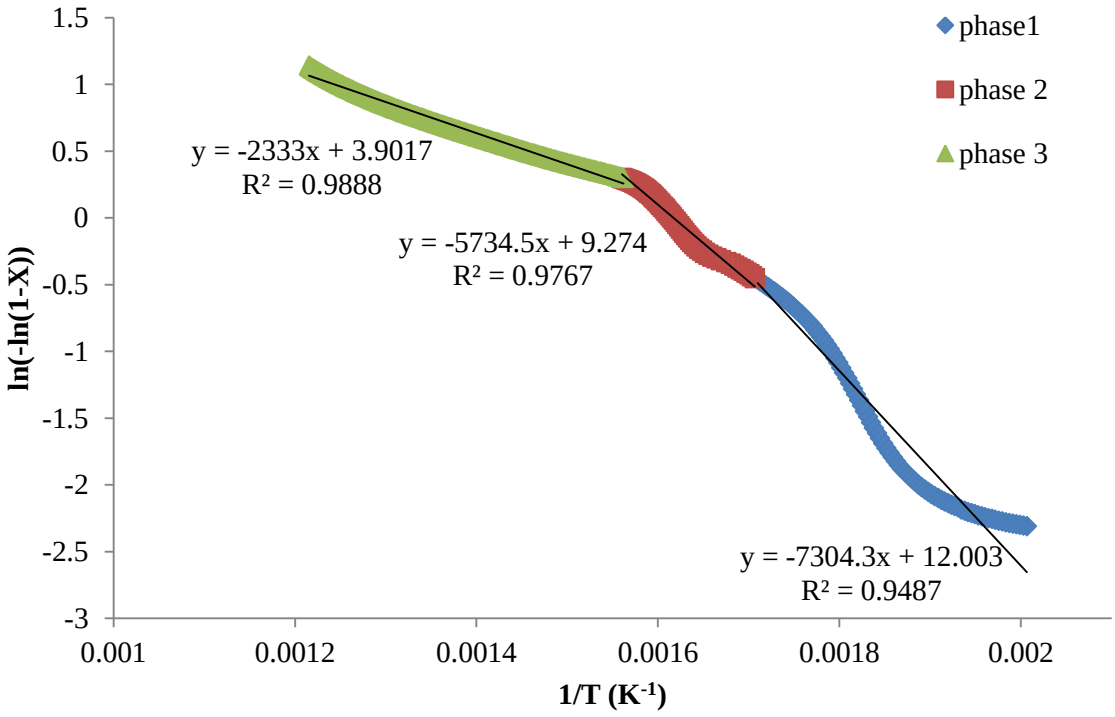

Figure 5.1 Kinetic graph of coconut shell at 20°Cmin-1

	Trend Line	Regression Coefficients
1st phase	y = -7304.3x + 12.003	0.9487
2nd phase	y = -5734.5x + 9.274	0.9767
3rd phase	y = -2333x + 3.9017	0.9888

Table 5-1 Trend line equations and Regression coefficients of coconut shell pyrolysis

	Activation energy (KJ/Mol)	Pre- exponential factor
1st phase	60.73	91343.22
2nd phase	47.68	4099.44
3rd phase	19.40	11.64
Average	**36.29**	

Table 5-2 Activation energy and pre-exponential factor of coconut shell pyrolysis

Table 5.1 shows the trend line equations and regression coefficient which has been obtained from the graph with different phase. The phases are determined from dtg graph. The initial phase that was degradation of moisture is neglected and the rest of degradation from active pyrolysis range is taken into account. By using the corresponding equations and regression coefficient of three phases, activation energy has been determined for coconut shell degradation and shown in Table 5-2.

5.3 Conclusion

From TGA, the value of 1/T and ln[-ln(1-X)] has been calculated and plotted by splitting with three phases, three different activation energy has been obtained at different rate of heating. From Table 5.2 it was observed that at 1st phase the activation energy is more as compared to the 2nd phase and 3rd phase. This may be due to the highest degradation of cellulose and hemicellulose at 1st stages so it required more energy for decomposition.

Chapter 6

Conclusion and Future Work

6. Conclusions and Future Work

Petroleum resources are getting consumed at an alarming rate and renewable resource like biomass is looked upon as a replacement since it produces liquid that can be used as a fuel or as feedstock to other valuable chemicals. In this report, the pyrolysis of a biomaterial - coconut shell is investigated. Coconut shell is a waste generated from consumption of coconut which is available in plenty from rural areas in India can compensate the current petroleum and energy crisis.

6.1. Conclusions

The characterization raw material i.e. coconut shell powder was carried.

TGA showed degradation of raw material around 300°C onwards hence this decided pyrolysis temperature range.

Using TG data, kinetic study was done. The activation energies for different phases were found out.

Pyrolysis of coconut shell was carried out for different temperatures. With increase in temperature, the liquid yield increased up to temperature of 575°C at which highest liquid yield of 49.5% is obtained. The solid residue quantity decrease continuously while non-condensable part decreased with increase in temperature up to 575°C, after which it increased.

Physical properties and chemical properties of liquid product produced by pyrolysis at 575°C were also carried out.

The FTIR showed presence of alcohol or phenol and other functional groups like aldehyde and ether. The result is consistent with the findings of GC-MS.

1HNMR analysis of bio oil shows that CH_3 CH_2 and CH attached to an aromatic ring are present in higher proportion.

GC-MS was carried out. Phenol is detected in highest amount and many phenol derivatives were detected.

XRD analysis showed the breaking of crystalline structures of cellulose by pyrolysis.

SEM images showed presence of pores on solid residue. This leads to making of activated carbon from the char.

Various physical properties analysis of bio-oil showed that it needs up gradation to be used as bio-diesel. The bio-oil can be used as feedstock to produce phenol and phenolic resins.

6.2. Future Work

This work can be extended to develop a process for upgrading bio oil or develop a separation process for phenolic fraction recovery from coconut pyrolysis bio-oil. This study can also be extended to production phenolic resins.

Phenolic resins are typically cross-linked polymeric resins. But because of phenol price and availability to that of petroleum, industrial products using phenolic resins are relatively expensive. Hence further study can be made to substitute petroleum based phenol in phenolic resins with cost effective phenols derived from coconut shell pyrolysis.

A. Effendi, H. Gerhauser and A.V. Bridgwater in their review paper have discussed some of the methods for separation of phenol fraction and production of phenolic resins from bio-oil [43]. Separations of phenols from wood tar were studied and carried out by dissolution of an oil phase in ethyl acetate and five stage alkaline extraction by Amen-Chen, et al., together with a primary conversion of the raw wood tar into a lighter oil [44]. The review on the fractionation processes towards obtaining syringols or phenolic-rich fraction from pyrolysis oil was given by Mohan et al. [36]. Quite complicated fractionation scheme for isolation of phenolic compounds was presented by Rusell et al., applying six contact stages with different solvents [45].

Upgrading of bio-oils to higher value transportation fuels requires de-oxygenation and reforming of most of the compounds present in the bio-oil. Because of the large amount of oxygen present there will be a loss in yield but this will be balanced against higher heating values. It is possible to upgrade bio-oil to hydrocarbon-like fuels via catalytic hydrotreating or cracking as these processes remove the oxygen in bio-oil and then reform the remaining carbon and hydrogen into hydrocarbon compounds.

Diebold et al. have investigated in situ cracking of promptly formed biomass pyrolysis vapours over zeolite cracking catalysts [46]. An alternate approach using catalytic hydrotreating showed more promise. Elliott et al. and others have been developing this approach to chemical upgrading [47]. Hence further study can be done to achieve better bio-oil upgrading using different catalysts in an economic way.

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